

# Thermal and Radiolytic Gas Generation from Washed AN-102 Sludge

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October 2002

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Test specification: TSP-W375-01-00002 Rev. 0  
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Test exceptions: none  
R&T focus area: Pretreatment  
Test Scoping Statement(s): B-86

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## Completeness of Testing

*This report describes the results of work and testing specified by TSP-W375-01-00002 Rev. 0 and TP-RPP-WTP-066 Rev 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.*

### Approved:

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Gordon H. Beeman, Manager  
WTP R&T Support Project

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Date

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G. Todd Wright, Manager  
Research and Technology

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Date

## Summary of Testing

This report summarizes progress made in evaluating mechanisms by which flammable gases are generated in washed Hanford Tank 241-AN-102 (AN-102) sludge based on the results of laboratory tests using actual sludge samples from Tank AN-102. Gas generation from the sludge sample was measured as a function of temperature with and without the application of an external radiation source ( $^{137}\text{Cs}$  capsule).

The objective of this work was to establish the composition ratio of gas generated in actual tank sludge due to chemical and radiolytic processes as a function of temperature. The gas-generation tests focused first on the effect of temperature on the composition and rate of gas generation. Generation rates of hydrogen, nitrous oxide, nitrogen, and methane increased with temperature, and the composition of the gas mixture produced varied with temperature. The gas-generation rate was examined at 45°, 60°, 75°, 90°, and 105°C.

Gas-generation tests on actual radioactive tank sludge were conducted at the High-Level Radio-chemistry Facility in the 325 Building (325A HLRF). Gas-generation measurements were made using reaction vessels and a gas manifold system similar to those used in earlier studies with simulated waste (Bryan and Pederson 1995) and described in earlier reports detailing work with actual waste (Bryan et al. 1996).<sup>(a,b)</sup> The self-dose rate from the radionuclide inventory of Tank AN-102 samples was calculated to assess the amount of radiolytically induced gas from internal radiation sources.

CH2M HILL Hanford Group requested that Battelle - Pacific Northwest Division (PNWD) measure the energetics of washed AN-102 solids to help assess the washed solids' reactivity hazard (Reynolds 2001). Hanford used the Babad et al. (1995) strategy to assess the reactivity hazards of stored organic-bearing high-level waste (Meacham 1997), and we employed the same basic strategy using enthalpy-calibrated differential thermal analysis (DTA) rather than differential scanning calorimetry (DSC) from room temperature to 500°C. We calibrated the DTA using known melting point standards. In the event that we saw an exothermic reaction producing >480 J/g dry waste, we analyzed the material with the Reactive System Screening Tool (RSST) after concurrence from Bechtel National Inc. (BNI).

The AN-102 washed solids exhibited exothermic behavior, but the heat released fell below the Hanford threshold criterion (480 J/g dry waste) measured by DSC (Babad et al. 1995). Because of this, we did not attempt to measure the enthalpy using the RSST. The heat measured was substantially less than the theoretical maximum, which is 320 J/g assuming reaction of the oxalate and total organic carbon content with nitrite and hydroxide.

Arrhenius treatment of the rate data yielded activation parameters for gas generation, as shown in Table S.1.

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(a) King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

(b) Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, WA.

**Table S.1.** Thermal and Radiolytic Rate Parameters for Gas Generation from Washed AN-102 Waste

	<b>H<sub>2</sub></b>	<b>N<sub>2</sub>O</b>	<b>N<sub>2</sub></b>	<b>CH<sub>4</sub></b>	<b>Overall rate</b>
E <sub>a</sub> , kJ/mol	63(±16)	111(±28)	58(±29)	71(±155)	109(±40)
A, mol/kg/day	3.81E+03	2.75E+11	3.30E+03	1.38E+03	2.09E+11
ln(A)	8(±5)	26(±10)	8(±10)	7(±51)	26(±14)
R <sup>2</sup>	0.928	0.915	0.835	0.415	0.856
G-value at 33,400 R/h	0.055 (±0.018)	0.062 (±0.013)	0.0495 (±0.016)	0.0005 (±0.0002)	0.145 (±0.051)
G-value at 2076 R/h	0.019 (±0.007)	0.039 (±0.013)	0.0495 (±0.016)	0.0005 (±0.0002)	0.145 (±0.051)

We generated gas in the presence of a 31,300 R/h (<sup>137</sup>Cs) external gamma source to measure the radiolytic G-values for gas generation. The effect of radiation was examined at 45°, 60°, 75°, 90°, and 105°C. The radiolytic G-values, in molecules per 100 eV, were determined to be 0.055 (±0.018) for hydrogen, 0.062 (±0.013) for nitrous oxide, 0.0495 (±0.016) for nitrogen, and 0.0005 (±0.0002) for methane.

This work was performed in accordance with the PNWD's quality assurance project plan, River Protection Program-Waste Treatment Plant (RPP-WTP) Technical Support Quality Assurance Project Plan, RPP-WTP-QAPJP Rev. 0, as approved by the RPP-WTP QA organization. The work was performed in accordance with applicable elements of NQA-1-1989 and NQA-2a-1990, subpart 2.7.

## Summary References

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Bryan SA, LR Pederson, CM King, SV Forbes, and RL Sell. 1996. *Gas-Generation from Tank 241-SY-103 Waste*. PNL-10978, Pacific Northwest National Laboratory, Richland, WA.

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Reynolds RA. 2001. "Energetics and Gas Generation Studies." Test Specification, TSP-W375-01-00002 Rev. 0, CH2M HILL Hanford Group, Inc., Richland, WA.

# Contents

Summary of Testing.....	iii
1.0 Introduction.....	1
2.0 Experimental Methods for Gas Measurements .....	3
2.1 Experimental Conditions and Equipment.....	3
2.2 Tank AN-102 Test Material .....	6
2.2.1 Tank AN-102 Sample History .....	6
2.2.2 Tank AN-102 Sample Compositing and Subsampling for Gas-Generation Tests.....	7
2.3 Self-Dose Rate from Radionuclide Inventory in AN-102 Samples.....	14
3.0 Gas Generation from Tank AN-102 Sludge Samples .....	15
3.1 Composition and Rates of Gas Generation from AN-102 Waste .....	15
3.1.1 Thermal Gas Generation from Tank AN-102 Waste Sample .....	15
3.1.2 Radiolytic Gas Generation from Tank AN-102 Waste .....	18
3.2 Thermal and Radiolytic Rate Parameters for Gas Generation from Tank AN-102 Waste .....	20
4.0 Energetics of AN-102 Washed Solids .....	25
4.1 Composition of Washed AN-102 Solids .....	25
4.2 Measurement Strategy .....	26
4.3 Results .....	26
5.0 Summary and Conclusions .....	29
6.0 References.....	31

## Figures

1	Reaction Vessel Used in Small-Scale Gas-Generation Tests .....	3
2	Diagram of Reaction Vessel Holder with Gamma Source Used in Gas-Generation Tests .....	4
3	Diagram of Pressure Manifold System Used in Gas-Generation Tests .....	4
4	Flow Diagram of AN-102 Tank Slurry Receiving, Homogenizing, and Subsampling .....	8
5	Sample Preparation Scheme for Washing AN-102 Samples Used in Gas-Generation Tests .....	11
6	Mixer Used to Homogenize AN-102 Material .....	12
7	AN-102 Material Being Blended within Homogenization Vessel with Inhibited Water .....	13
8	Homogenized AN-102 Material after Third Wash Step and before Liquid Decant .....	13
9	Percent Composition of Major Gas Products from Thermal Reactions of AN-102 Waste as a Function of Temperature .....	17
10	Rates of Total Gas Generated from Washed AN-102 Waste under Self-Radiolysis and High-Dose Conditions .....	22
11	Formation of Major Gas Components from Washed AN-102 Waste under Self-Radiolysis Conditions .....	22
12a	Tank AN-102 Thermal and Radiolytic Gas-Generation Rates for Hydrogen and Nitrogen .....	23
12b	Tank AN-102 Thermal and Radiolytic Gas-Generation Rates for Nitrous Oxide and Methane .....	24
13	Average Thermal Behavior of Washed AN-102 Solids from 100° to 500°C .....	27

## Tables

1	Sample Masses and Vessel Volumes Used in Small-Scale Gas-Generation Tests Using Washed Tank AN-102 Wastes .....	5
2	AN-102 HLW Samples Received.....	7
3	AN-102 As-Received Composite Subsamples Collected from Homogenization Vessel.....	10
4	Calculated Self-Radiolysis Dose Rates from AN-102 Waste Within a Small Reaction Vessel and Large Tank .....	14
5	Mole Percent Composition Thermal Gas Sampled and Gas Formed and Heating Times of Duplicate Systems at Three Temperatures .....	16
6	Gas-Generation Rates from Thermal Treatment of Washed AN-102 Material in the Absence of an External Radiation Source.....	18
7	Mole Percent Composition of Radiolytic Gas Sampled and Formed and Heating Times of Duplicate Systems at Five Temperatures.....	19
8	Gas-Generation Rates from Radiolytic Treatment of Tank AN-102 Material in the Presence of an External Radiation Source .....	20
9	Thermal and Radiolytic Rate Parameters for Gas Generation from Washed AN-102 Waste .....	23
10	Measured Composition of AN-102 Washed Solids .....	26
11	Thermal Behavior of AN-102 as Measured by DTA/TGA .....	28

## 1.0 Introduction

This report describes research performed to measure gas generation from actual sludge taken from a composite sample of Tank 241-AN-102 (AN-102).<sup>(a)</sup> The AN-102 sludge was washed with inhibited water (0.01 M NaOH) before testing to simulate the expected pretreatment processing. Battelle – Pacific Northwest Division (PNWD) is conducting the thermal and radiolytic gas generation from this washed Tank AN-102 sludge for the Office of River Protection (ORP) Waste Treatment Plant (WTP). The work was detailed in the *Energetics and Gas Generation Test Plan*,<sup>(b)</sup> which was written in response to the CH2M HILL Test Specification (Reynolds 2001). There were no deviations from the stated test plan.

The gas-generation tests on Tank AN-102 samples focus first on finding the effects of temperature and second on the results of irradiating AN-102 samples with an external source (<sup>137</sup>Cs capsule). The tank sludge samples and radiation source are contained in a hot cell. Gas measurement equipment is contained in an adjacent hood attached to the reaction vessels by small-diameter (0.0058 cm inside diameter) stainless steel tubing. The tests establish gas-generation rates from actual sludge samples as a function of temperature with and without irradiation. From these results, thermal activation energies can be calculated that allow gas-generation rates at other temperatures to be calculated. G-values for the radiolytic gas-generation component are also derived from these data.

To assess the effects of temperature on the gas generation from washed AN-102 sludge, experiments were performed in duplicate at five temperatures (45°, 60°, 75°, 90°, and 105°C), or 10 reactions total. The effects of radiation on gas generation were assessed by repeating the thermal experiment in the presence of an external <sup>137</sup>Cs gamma capsule. The irradiation experiments were performed in duplicate at the same five temperatures. The thermal tests provide activation energies for gas generation (Laidler 1987); the radiolytic experiments provide G-values for gas generation (Spinks and Woods 1990). These parameters allow estimation of gas-generation rates of the principal gas components within washed AN-102 sludge under current and future storage conditions.

Section 2 of this report describes the gas-generation test samples and the experimental conditions and equipment used for the tests. Section 3 presents the results and discusses the gas-generation experiments. Section 4 contains the energetic measurements of AN-102 washed solids, Section 5 is a summary, and Section 6 contains the cited references. Appendix A contains a copy of the test plan outlining the work scope for this report.<sup>(b)</sup> Appendix B contains the test instruction with specific details of implementation of the test plan. Appendix C contains the results of analytical measurements performed on AN-102 waste samples.

The objectives of this testing were to 1) prepare washed solids from AN-102 suitable for use within this task; 2) perform thermal and radiolytic experiments on washed solids from AN-102 under thermal and irradiated conditions, and 3) perform energetic testing on washed solids from AN-102. The data within this report will be used to provide information on the gas-generation capacity and reactivity of

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(a) Hanford waste tanks are designated with the prefix 241-. In this report, as in common usage, the prefix is omitted.

(b) Bryan SA and RD Scheele. 2001. Battelle Test Plan: *Energetics and Gas Generation*. TP-RPP-WTP-066, Pacific Northwest National Laboratory, Richland, WA.



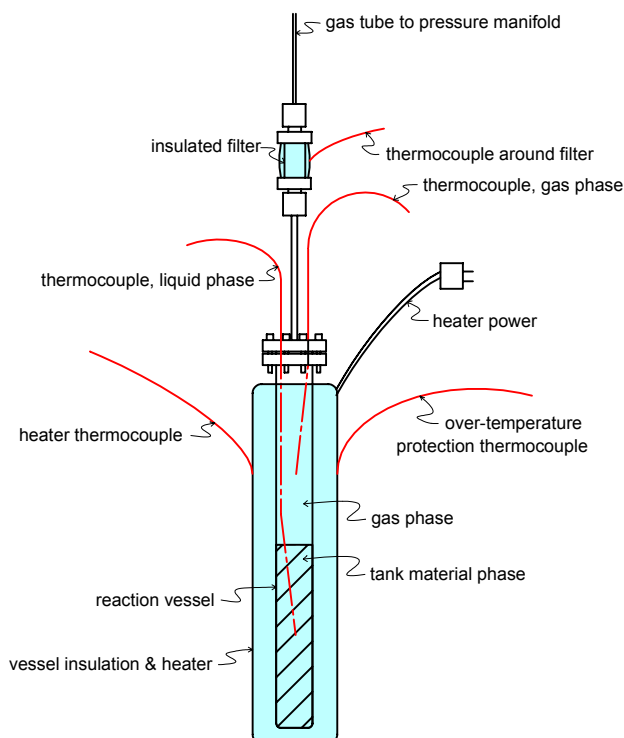
Tank AN-102 sludge material. The gas-generation studies explore the rate at which gases will be generated under any given thermal and radiolytic conditions. These tests will help us understand certain safety concerns and provide information on potential emissions to the pretreatment vessel off-gas ventilation system.

## 2.0 Experimental Methods for Gas Measurements

Gas-generation tests on actual radioactive tank sludge were conducted in the 325 Building High-Level Radiation Facility (325A HLRF). A description of the experimental conditions is given in Section 2.1. A description of the Tank AN-102 test material and washing procedure is given in Section 2.2. The self-dose rate from the radionuclide inventory of Tank AN-102 samples was calculated to assess the amount of radiolytically induced gas from internal radiation sources. These calculations are given in Section 2.3.

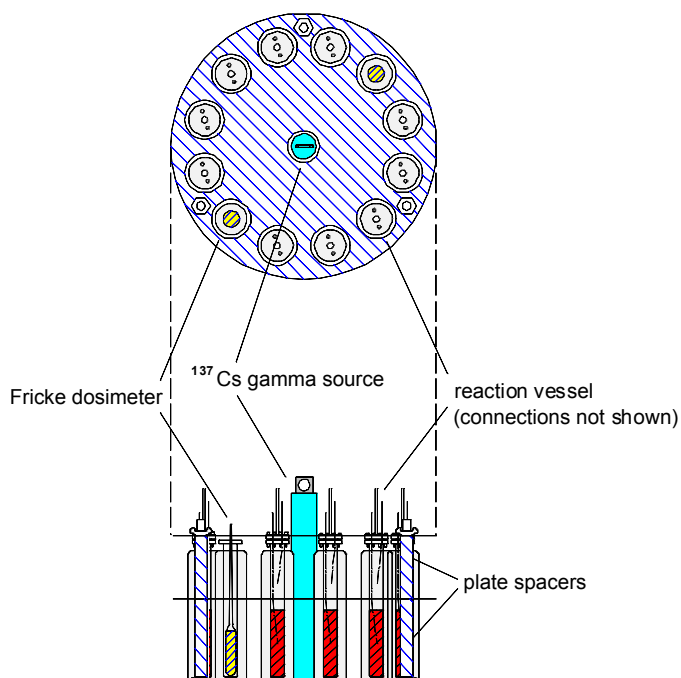
### 2.1 Experimental Conditions and Equipment

Gas-generation measurements were made using reaction vessels and a gas manifold system similar to those used in earlier studies with simulated waste (Bryan and Pederson 1995) and described in earlier reports detailing work with actual waste (Bryan et al. 1996; King et al. 1997).<sup>(a)</sup> Each vessel has a separate pressure transducer on the gas manifold line. The entire surface of the reaction system exposed to the sludge sample is stainless steel, except for a gold-plated copper gasket sealing the flange at the top of the reaction vessel. Figure 1 is a drawing of the reaction vessel showing the placement of the thermocouples within and at various locations on the outside of the reaction vessel. The location of reaction vessels within a carousel-style holder is depicted in Figure 2. The arrangement of the reaction vessels



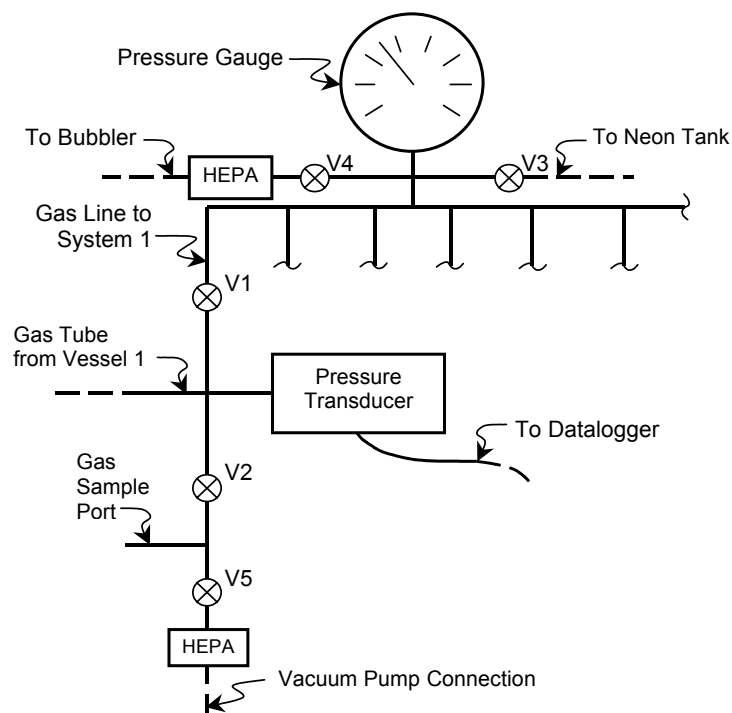
**Figure 1.** Reaction Vessel Used in Small-Scale Gas-Generation Tests

(a) Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, WA.



**Figure 2.** Diagram of Reaction Vessel Holder with Gamma Source Used in Gas-Generation Tests

near the  $^{137}\text{Cs}$  gamma capsule (in the center of the carousel) and Fricke dosimeters (Spinks and Woods 1990) (when used) are also shown. Figure 3 is a schematic diagram of the gas manifold system. Temperatures and pressures are recorded every 10 seconds on a Campbell Scientific CR10 datalogger; an average of the data is taken every 20 minutes and saved in a computer file.



**Figure 3.** Diagram of Pressure Manifold System Used in Gas-Generation Tests

The reaction vessels are cylinders of 316L stainless steel. The reaction space of the vessel is approximately  $\frac{3}{4}$  inch in diameter and 5 inches high. Each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body of the reaction vessel, one for temperature control and one for over-temperature protection. Two thermocouples were inserted through the lid. The thermocouple centered in the lower half of the vessel monitors the temperature of the liquid phase; the one centered in the upper half monitors the gas phase temperature within the reaction vessel. The reaction vessels were placed in a hot cell and connected by small inner diameter tubing (0.1016 cm ID) to the gas manifold outside the hot cell. A stainless steel filter (60-micrometer pore size, Nupro<sup>®</sup>) protected the tubing and manifold from contamination. A thermocouple was attached to this filter as well.

The total gas in the system was calculated using the ideal gas law relationship from the pressure, temperature, and volume of the parts of the apparatus having different gas phase temperatures:  $\text{moles}_{\text{total}} = \text{moles}_{\text{vessel}} + \text{moles}_{\text{filter}} + \text{moles}_{\text{manifold and tubing}}$ . The manifold and filter volumes were determined from pressure/volume relationships using a calibrated gas manifold system. The manifold volume (the pressure sensor, valves, and miscellaneous fittings) was 3.99 mL, the filter volume 1.34 mL, and the tubing volume 4.45 mL (by calculation). The cap stem (the tube from vessel to filter) has a volume of 0.20 mL to adequately account for pressure-temperature effects of the gas within the cap stem. Half of that volume was added to the filter volume for a total of 1.44 mL; and half of that volume was added to the vessel volume. The volume of each vessel was determined gravimetrically by filling it with water. These volumes are recorded in Table 1 along with the mass of sludge added to each vessel and the gas-phase volume in the vessel after the sample was added. The reproducibility of the molar gas determination using this manifold system has been determined experimentally. The relative error for measuring moles of gas with the system has been determined. A detailed discussion can be found in Bryan et al. (1996). The relative standard deviation for quantitative gas phase measurements conducted over time and temperature ranges similar to that of the gas-generation tests was typically less than 2%.

An atmospheric pressure gauge was attached to the datalogger. The pressure in each system is given as the sum of atmospheric pressure and relative pressure in each system. Neon, because it leaks more

**Table 1.** Sample Masses and Vessel Volumes Used in Small-Scale Gas-Generation Tests with Washed Tank AN-102 Wastes

Thermal										
System	1	2	3	4	5	6	7	8	9	10
Temperature	45°C	45°C	60°C	60°C	75°C	75°C	90°C	90°C	105°C	105°C
Sample mass, g	18.17	18.35	17.97	18.55	17.98	17.58	18.30	18.41	18.07	17.98
<i>Vessel Volumes</i>										
gas phase, mL	18.60	18.45	18.77	18.30	18.75	19.04	18.47	18.40	18.60	18.69
total, mL	32.54	32.52	32.56	32.54	32.55	32.53	32.51	32.53	32.47	32.49
Radiolytic										
System	11	12	13	14	15	16	17	18	19	20
Temperature	45°C	45°C	60°C	60°C	75°C	75°C	90°C	90°C	105°C	105°C
Sample mass, g	18.62	17.71	18.13	18.07	17.51	17.96	18.27	17.90	17.98	17.88
<i>Vessel Volumes</i>										
gas phase, mL	18.20	18.96	18.64	18.64	19.10	18.75	18.54	18.77	18.72	18.81
total, mL	32.49	32.55	32.55	32.51	32.54	32.53	32.56	32.51	32.52	32.53

slowly than helium from the system, was used as cover gas. The neon was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant enough to warrant correction.

At the start of each run, each system was purged by at least three cycles of pressurizing with neon at 45 psi (310 kPa) and venting to the atmosphere. The systems were at atmospheric pressure, about 745 mm Hg (99.3 kPa), when sealed. The sample portion of the manifold was isolated (valves V1 and V2 closed) (see Figure) for the remainder of the run. The vessels were then heated, adjusting the set points to keep the material within 1°C of the desired liquid phase temperatures. The temperature of the gas phase was 5 to 25°C lower than that of the sample liquid phase.

At the end of each run, the vessels were allowed to cool overnight, then a sample of the gas was taken for mass spectrometry analysis. The metal gas collection bottles were equipped with a valve and had a volume of approximately 75 mL (about four times the volume of the gas reaction system). The bottle, after being evacuated overnight at high vacuum, was attached to the gas sample port. Air was removed from the region between valves V2 and V5 (Figure 3) using a vacuum pump, then the gas sample was taken. After the collection bottle was removed, the bottle and sample port were surveyed for radioactive contamination. No contamination was found during these experiments. The reaction vessel was purged again with neon after each sampling event and before the next reaction sequence. For the irradiation experiments, the gamma source was removed from the gas-generation apparatus during gas-sampling events so that the length of time of heating was the same as the length of time of irradiating.

Analysis of the composition of the gas phase of each reaction vessel after each run was performed according to analytical procedure PNNL-MA-599 ALO-284 Rev. 1. The amount of a specific gas formed during heating is given by the mole percent of each gas multiplied by the total moles of gas present in a system. Duplicate samples, which were run in separate reaction vessels and sampled independently at each temperature, were used to assess the reproducibility and uncertainty of the rate parameters.

Gases in the reaction system are well mixed. The measured amount of argon in gas samples is an indicator of how much nitrogen from air has leaked into the system (the N<sub>2</sub>:Ar ratio in air is 83.6:1). The nitrogen produced in the vessel is the total nitrogen minus atmospheric nitrogen. The solubilities of nitrogen, hydrogen, methane, and nitrous oxide gases have been measured on simulated waste systems similar in composition to the liquid in AN-102 sludge (Pederson and Bryan 1996). Less than 0.01% of these gases dissolve in the condensed phase, so loss of these gases due to solubility is negligible.

## **2.2 Tank AN-102 Test Material**

The AN-102 sludge sample used in gas-generation testing is a blend of samples received and processed by PNWD in FY 2000 and 2001. The sample history is detailed in Section 2.2.1. The compositing and subsampling of Tank AN-102 samples for gas-generation tests is detailed in Section 2.2.2.

### **2.2.1 Tank AN-102 Sample History**

Thirty samples were obtained from Hanford Tank AN-102 in August 2000. The samples were taken from riser 22 at six different tank waste heights. The samples were shipped to the 222-S Laboratory in Hanford's 200 West Area and stored. PNWD received 27 of these samples from the 222-S Laboratory in

November 2000 but used only eight for characterization and process testing. (The other 19 samples received in this shipment, some containing slurry and others supernatant only, were not used to support this work.) These eight samples were obtained at the sampling location 190 cm (76 inches) from the bottom of the tank at the sludge/supernatant interface and contained a large (nominally 50% by volume) solids/sludge fraction. The samples were not necessarily representative of the entire tank contents.

The net weight of each of the high-level-waste (HLW) samples retrieved from Tank AN-102 was 600 to 700 g.<sup>(a)</sup> Each sample arrived in a 500-mL bottle and consisted of wet solids plus supernatant. Upon receipt at the HLRF, the AN-102 samples were inspected visually, and the inspection was documented.<sup>(b)</sup> All bottles and lids were in good condition. All samples were similar in appearance, comprising a large amount of light-brown settled solids and a dark brownish/black liquid. An organic layer could not be discerned because of the dark color of the supernatant. No specific crystalline phases were apparent. Inspection results are provided in Table 2.

**Table 2.** AN-102 HLW Samples Received<sup>(a)</sup>

Bottle Label	222-S ID	Net Mass Recovered, g	Visual Appearance Settled Solids	Approximate Solids Volume, mL	Visual Appearance Supernatant	Approximate Supernatant Volume, mL
2AN-00-21	S00T001598	671	Light brown solids	100	Dark brown to black	400
2AN-00-24	S00T001602	669	Light brown solids	275	Dark brown to black	225
2AN-00-25	S00T001664	658 <sup>(b)</sup>	Light brown solids	100	Dark brown to black	400
2AN-00-26	S00T001665	687	Light brown solids	300	dark brown to black	200
2AN-00-27	S00T001666	669	Light brown solids	200	Dark brown to black	300
2AN-00-28	S00T001667	673	Light brown solids	200	Dark brown to black	300
2AN-00-29	S00T001662	670	Light brown solids	300	Dark brown to black	200
2AN-00-30	S00T001663	690	Light brown solids	250	Dark brown to black	250
Total mass received		5388				
(a) No crystalline phases were present in any of the samples received.						
(b) 137 g of supernatant were removed from this sample, leaving 521 g. This supernatant was used for Sr/TRU (transuranic) removal testing.						

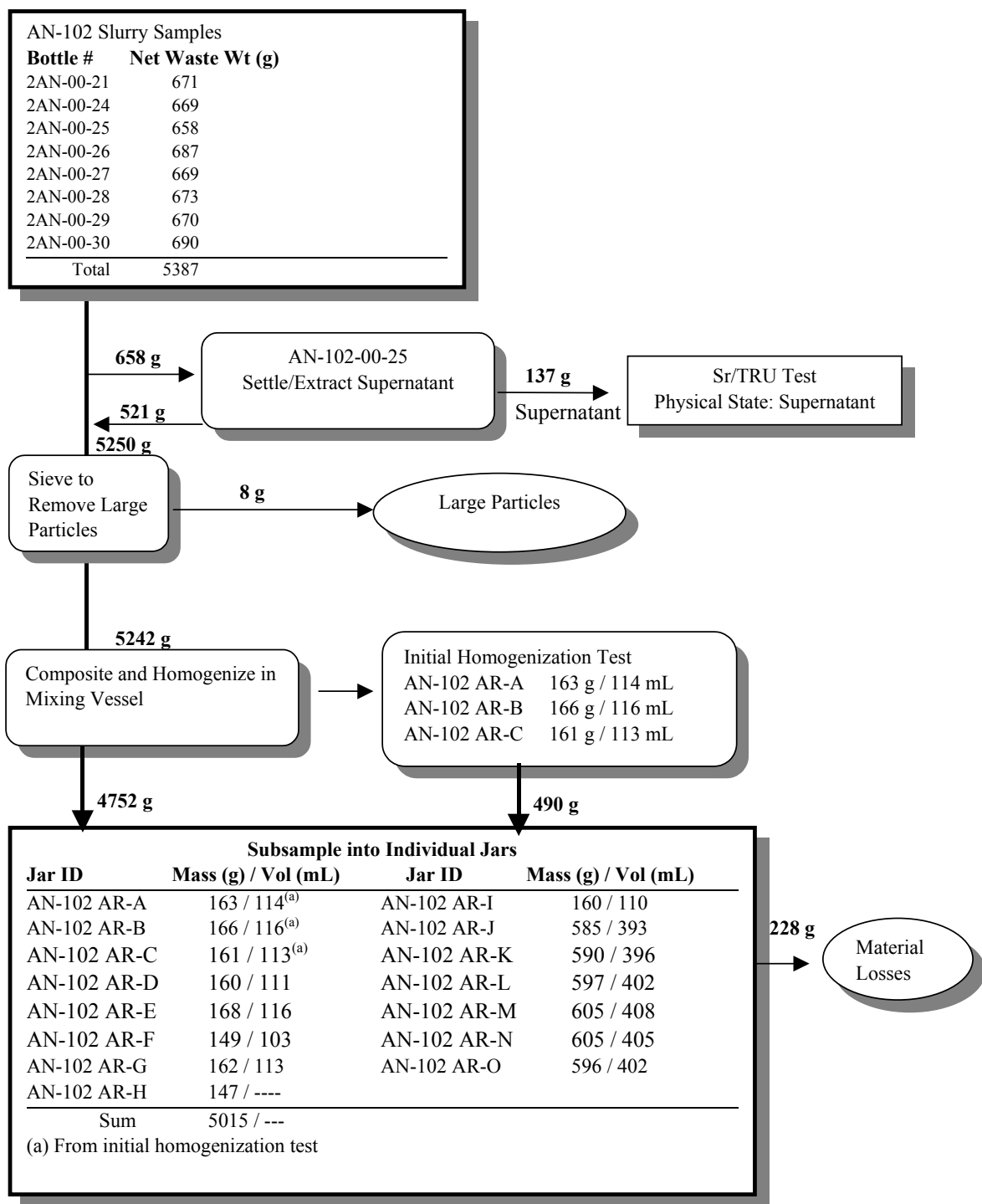
## 2.2.2 Tank AN-102 Sample Compositing and Subsampling for Gas-Generation Tests

The objective of compositing the AN-102 samples is to provide homogeneous feed to tasks within the project. The feed is used to support characterization as well as process testing. The homogenization and subsampling are summarized in Figure 4.<sup>(c)</sup>

(a) Seidel CM to DJ Hart. November 2, 2000. "Shipment of AN-102 to Pacific Northwest National Laboratory." Internal memorandum 8G00-CMS-00-028, Fluor Hanford Inc., Richland, WA.

(b) Bredt P. 2000. PNNL Test Instruction "AN-102 Sample Inspection." TI-41500-009, PNNL, Richland, WA.

(c) Urie MW, SK Fiskum, JA Campbell, OT Farmer, LR Greenwood, EW Hoppe, GM Mong, CZ Soderquist, RG Swoboda, MP Thomas, and JJ Wagner. 2001. *Chemical Analysis and Physical Property Testing of 241-AN-102 Tank Waste Supernatant and Centrifuged Solids*. WTP-RPT-020, PNWD, Richland, WA.



**Figure 4.** Flow Diagram of AN-102 Tank Slurry Receiving, Homogenizing, and Subsampling

Before compositing, 137 g of supernatant was removed from bottle number 2AN-00-25 to conduct Sr/TRU process testing (these results will be presented in a separate report). Then all materials in the eight bottles were passed through a 2.38-mm (3/32-inch) sieve to remove large particles. The transferred material was collected in an 8-L stainless steel mixing vessel. Clumps of agglomerated material were retained on the sieve. Most of this material was pushed through the sieve with a glass stopper. A total of 7.8 g (mass after more than eight hours of drying time) of large particles could not be crushed with a glass stopper and were trapped on the screen. Characteristics of these particles were not inconsistent with gravel; however, definitive identification could not be made. The particles were later discarded.

The AN-102 HLW was homogenized in the mixing vessel equipped with a dual-bladed impeller. Material was stirred with the impeller for about 70 minutes at 31.5°C (the ambient hot cell temperature) for thorough homogenization. With the impeller running, a 100-mL portion was removed through the 3/4-inch valve on the bottom of the vessel to flush the valve and connecting tube. This flush material was poured back into the mixing vessel. Initially, three 100-mL samples collected from the mixing vessel for homogenization evaluation were placed into volume-graduated glass jars numbered AN-102 AR-A through AN-102 AR-C (“AR” indicates “as-received”). The volume percent (vol%) settled solids was determined on each and found to be consistent within 1%. The remaining contents of the mixing vessel were stirred and collected into 12 additional volume-graduated glass jars labeled AN-102 AR-D through AN-102 AR-O. Sample AN-102 AR-H was used immediately for physical properties testing. The remaining 14 jars were left undisturbed for six to seven days and showed no signs of crystallization of the liquid phase or organic layer formation following the hold time.

The total volume of material in each of the 14 jars and the volume of settled solids were recorded after the seven-day settling period and used to calculate the vol% settled solids. Table 3 lists the calculated mass, volume, and vol% settled solids for each subsample. According to the test specification, the absolute standard deviation of the vol% settled solids of the 14 subsamples must be less than 5%. Constant vol% settled solids is one measure of homogeneity. The average vol% settled solids of as-received homogenized subsamples was 70% with a standard deviation of  $\pm 2.5\%$ . As shown in Table 3, the subsamples collected in the jars from the compositing vessel met the test specification for homogeneity.

Subsamples AN-102 -A, -B, -C, -D, -F, -G, and -I were selected for inorganic, radiochemical, and organic characterization analyses and were transferred from the HLRF to the Shielded Analytical Laboratory (SAL) for processing and analysis. Subsamples AN-102 AR-J, -K, -L, -M, and -N were selected for gas-generation testing.

The sample preparation scheme used to prepare the AN-102 samples for gas-generation testing is shown in Figure 5. The sample preparation is described in test instruction TI-RPP-WTP-074 Rev. 1.<sup>(a)</sup> The general plan was to take a representative composite sample of AN-102 (as-received from Test Plan BNFL-TP-41500-015), separate the standing liquid settled by gravity from this sample, then wash the sample with inhibited water (0.01 M NaOH) three times. Each inhibited water wash was gravity settled and the supernate decanted. There was mass loss due to water evaporation during the mixing, settling, decanting stages in the hot cell, consistent with that observed in other tank waste homogenizations.<sup>(b)</sup>

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(a) Bryan SA and RD Scheele. 2001. *Energetics and Gas Generation*. TP-RPP-WTP-066, PNWD, Richland, WA.  
(b) Bredt, PR. 2001. *AZ-101 Sample Homogenization*. TI-RPP-WTP-095 Rev. 0, PNWD, Richland, WA.

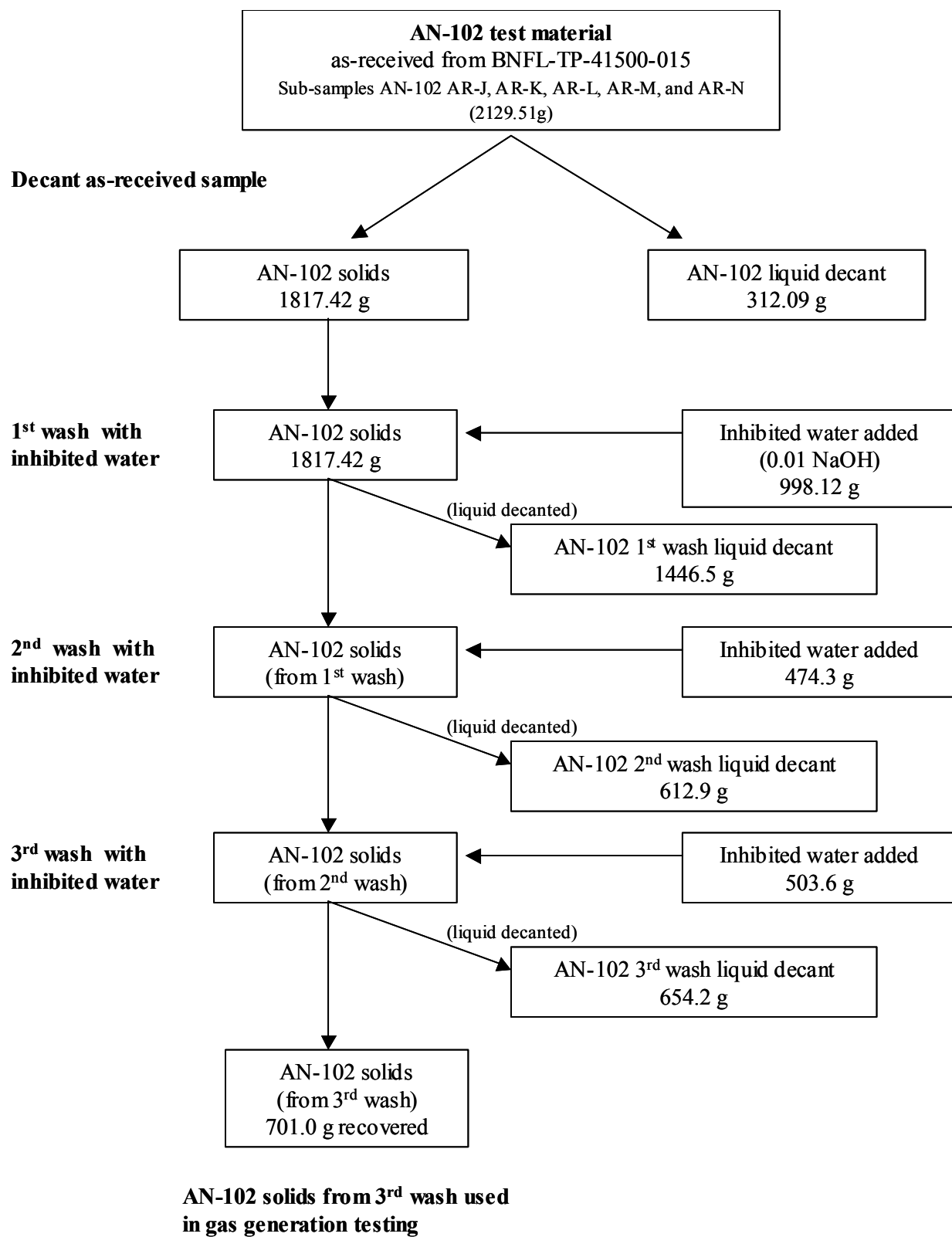


**Table 3.** AN-102 As-Received Composite Subsamples Collected from Homogenization Vessel

Jar ID	Sample Mass (g)	Sample Volume (mL)	Vol% Settled Solids (visual)
AN-102 AR-A	163	114	72.8
AN-102 AR-B	166	116	72.4
AN-102 AR-C	161	113	73.5
AN-102 AR-D	160	111	69.8
AN-102 AR-E	168	116	71.1
AN-102 AR-F	149	103	72.8
AN-102 AR-G	162	113	70.8
AN-102 AR-H	147	NA	NA
AN-102 AR-I	160	110	71.8
AN-102 AR-J	585	393	67.7
AN-102 AR-K	590	396	70.1
AN-102 AR-L	597	402	68.4
AN-102 AR-M	605	408	68.1
AN-102 AR-N	605	405	67.2
AN-102 AR-O	596	402	65.4
Average			70.1
Standard Deviation ( $1\sigma$ )			2.5
NA- Not available. Sample H was immediately removed for physical testing, so data on settled volumes were not collected.			

The homogenization of the AN-102 sludge sample was performed using a mixing vessel equipped with a dual-bladed impeller (Figure 6). Material was stirred with the impeller for one hour at 31.5°C (the ambient hot cell temperature) to thoroughly homogenize the material. With the impeller running, a 100-mL portion was removed through the  $\frac{3}{4}$  inch valve on the bottom of the vessel to flush the valve and connecting tube. This flush material was poured back into the mixing vessel. It was evident from observing the mixing action that the sample was well mixed. Figure 7 is an in-cell photo showing the blending of the AN-102 sample in the homogenization vessel. After each of three washes, the sample was gravity settled and the standing supernate decanted (see Sample Preparation Scheme in Figure 5).

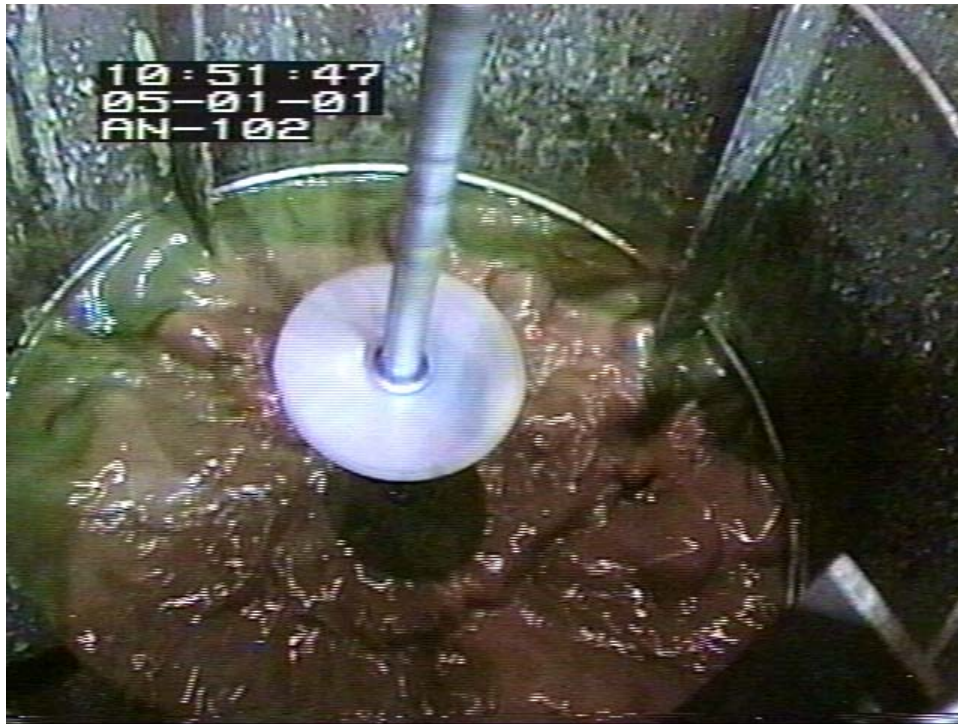
Figure 8 shows the AN-102 samples after the third wash, after they were allowed to settle overnight and before the supernate was decanted from the surface of the solids. The solids obtained after this third decant were used in the gas-generation tests in this report.



**Figure 5.** Sample Preparation Scheme for Washing AN-102 Samples Used in Gas-Generation Tests



**Figure 6.** Mixer Used to Homogenize AN-102 Material (taken with digital camera inside the hot cell using incandescent light)



**Figure 7.** AN-102 Material Being Blended within Homogenization Vessel with Inhibited Water Added (taken with digital camera inside the hot cell using incandescent light)



**Figure 8.** Homogenized AN-102 Material after Third Wash Step and before Liquid Decant. The samples were allowed to settle overnight before the supernate was decanted. Collectively, the glass jars contain 701g of AN-102 washed solids after liquid decant (taken with digital camera inside the hot cell using incandescent light)

## 2.3 Self-Dose Rate from Radionuclide Inventory in AN-102 Samples

The self-dose rate for Tank AN-102 material in the gas-generation reaction vessel was calculated based on the measured chemical and radiochemical content of the test sample. The self-dose rate is needed to correct for radiolytic generation from self-radiolysis of the sample. The measured radionuclides are  $^{137}\text{Cs}$  (99.9  $\mu\text{Ci/g}$ ),  $^{90}\text{Sr}$  (828.8  $\mu\text{Ci/g}$ ),  $^{60}\text{Co}$  (0.046  $\mu\text{Ci/g}$ ),  $^{154}\text{Eu}$  (2.32  $\mu\text{Ci/g}$ ), and  $^{155}\text{Eu}$  (1.42  $\mu\text{Ci/g}$ ). Sources of measured alpha radiation are  $^{241}\text{Am}$  (1.96  $\mu\text{Ci/g}$ ),  $^{243/244}\text{Cm}$  (0.068  $\mu\text{Ci/g}$ ), total alpha (2.60  $\mu\text{Ci/g}$ ); the difference between the sum of Cm and Am compared to total alpha is presumably due to the presence of Pu activity in the sample. Chemical constituents include fluoride, (0.17 wt%), chloride (0.07 wt%), nitrite (1.79 wt%), nitrate (4.08 wt%), phosphate (0.28 wt%), sulfate (0.49 wt%), oxalate (8.92 wt%), hydroxide (0.55 wt%), aluminum (13.13 wt%), sodium (16.3 wt%), chromium (0.96 wt%), manganese (0.15 wt%), and water (52.5 wt%). The chemical and radiochemical data are reported on a wet, washed solids basis..

The dose rate in a reaction vessel was calculated by the PNWD Dosimetry Research and Technology Group using MCNP version 4B (Monte Carlo N-Particle Transport Code System) (Briesmeister 1997). This program uses the Monte Carlo method, in which radiation is emitted in random directions from random locations in the sample. The probability of the radiation being either absorbed or scattered by the sample and of its being reflected from the container wall back into the sample is known. The reaction vessel (316L stainless steel construction) was modeled as a cylinder with 0.035-inch-thick steel walls, inside diameter of 0.680 inch, height 5.5 inches, base thickness 0.185 inch, and lid thickness 0.210 inch. Input to the program includes the composition of the walls, the composition of the bulk of the sample, and the radionuclides present. The output is the amount of radiation absorbed by the sample averaged over its entirety. Table 4 contains the calculated dose rates for the waste sample in the small reaction vessel (~32.5 mL). Using the same waste volume for comparison, the dose rate was calculated for a much larger vessel, a tank 10 m high and 10 m in diameter (758  $\text{m}^3$ ). A large difference exists in the gamma dose rate term due to edge-loss of gamma in the small reaction vessel configuration. Because essentially all the beta and alpha radiation is absorbed (or reflected back) in the sample and most of the dose is from beta sources, the total dose rate from the small vessel (2076 R/h) is fairly close to the dose rate calculated from the much larger vessel.

The dose rate in a reaction vessel with the  $^{137}\text{Cs}$  capsule placed in the middle of the vessel holder was determined by Fricke dosimetry, as described in King et al. (1997). The externally applied dose rate from the  $^{137}\text{Cs}$  capsule measured within the reaction vessel was 31,300 R/hr (average of four determinations) with a relative standard deviation of 18%. Correcting for the half-life of  $^{137}\text{Cs}$  (30 yr), this measurement is consistent with that made by King et al. (1997) for the same  $^{137}\text{Cs}$  gamma capsule. When the  $^{137}\text{Cs}$  gamma capsule was used, the dose rate received by the sample from external (31,300 R/hr) and internal (2076 R/hr) sources totaled 33,400 R/hr.

**Table 4.** Calculated Self-Radiolysis Dose Rates from AN-102 Waste in a Small Reaction Vessel and Large Tank (R/hr)

	Gamma	Beta	Alpha	Total
<b>Vessel</b>	5	2,044	27.2	2,076
<b>Tank</b>	122	2,044	27.2	2,193

### **3.0 Gas Generation from Tank AN-102 Sludge Samples**

Hanford tank waste produces gas as a function of the thermal and radiolytic aging of its components. To assess the relative contributions of thermal and radiolytic components, gas generation was measured from washed Tank AN-102 material under both thermal and radiolytic conditions. By isolating and measuring these components of gas generation, we can predict the gas-generation behavior of the waste under current tank conditions or under other conditions that may arise over time.

The percent composition and generation rates for gas generation under thermal conditions and radiolytic conditions are described in Section 3.1. Thermal activation parameters from standard Arrhenius treatment of the thermal experiments and G-value determinations from the radiolytic experiments are reported in Section 3.2.

#### **3.1 Composition and Rates of Gas Generation from AN-102 Waste**

Two sets of measurements were made on washed Tank AN-102 material, one in the presence of (radiolytic) and one in the absence of (thermal) external radiation. The measurements were run in duplicate at five temperatures, requiring 10 reaction vessels for each set of measurements. Both thermal and radiolytic measurements were made at 45°, 60°, 75°, 90°, and 105°C. Each vessel was loaded with the washed Tank AN-102 composite. Gas samples were taken from the vessels periodically. After each gas sample was taken, the vessel was purged with neon gas to remove previously generated gases before resuming gas generation. Gas-generation rates were determined for each gas sample from the heating time, the percent composition of the gas, the total moles of gas in each system when the sample was taken, and the mass of tank material present in each reaction vessel. Section 3.1.1 presents the thermal results, and Section 3.1.2 presents the radiolytic results.

##### **3.1.1 Thermal Gas Generation from Tank AN-102 Waste Sample**

This section contains the thermal gas-generation data produced by heating material in duplicate reaction vessels at 45°, 60°, 75°, 90°, and 105°C in the absence of external radiation. The total amount of gas produced versus heating time was calculated for all 10 reaction vessels. To obtain separate rates for each gas present, gas samples were analyzed by mass spectroscopy. The mole percent composition of these gas samples is given in Table 5. Of more interest are the relative amounts of gases generated, which are presented in the shaded areas. The composition of gas formed during heating is derived from the composition of sampled gas by excluding the neon cover gas, argon, nitrogen from atmospheric contamination, and oxygen. For example, if analysis found 80% neon, 15% nitrous oxide, and 5% hydrogen, the composition of gas formed by excluding neon would be 75% N<sub>2</sub>O and 25% H<sub>2</sub>. The uncertainties in all the entries in this table are approximately plus or minus one in the last digit.

In the tables of percent composition and rates, a run number and a letter identify the reaction vessel and the gas-sampling event, respectively. For example, entries for runs 1a and 2a give data at the first gas-sampling event for vessels 1 and 2, which happen to be duplicates at 45°C.

**Table 5.** Mole Percent Composition Thermal Gas Sampled (including Ne) and Gas Formed (shaded), and Heating Times of Duplicate Systems at Three Temperatures (no external radiation source)<sup>(a)</sup>

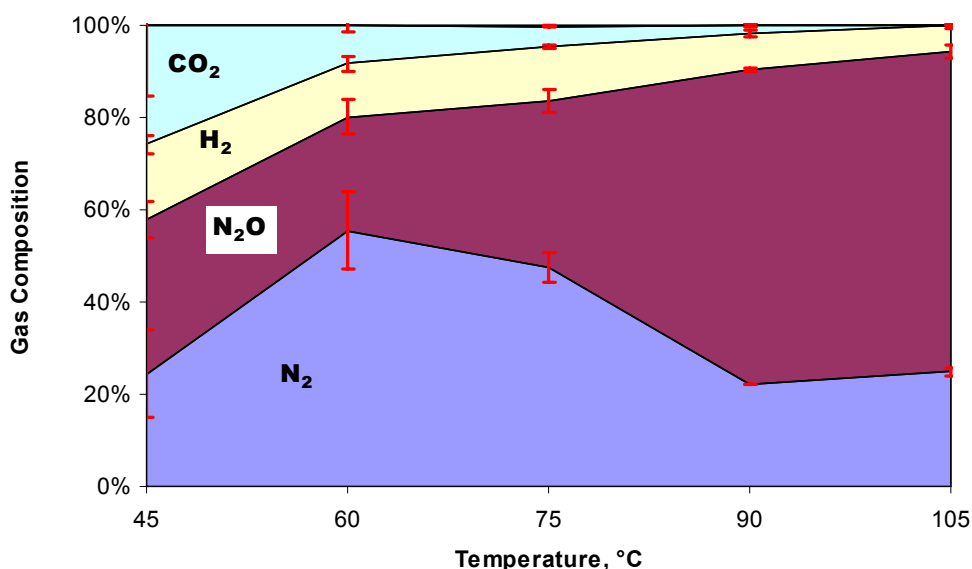
Mole Percent of Gas Formed at 45°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
1a	99.57	0.004	0.022	0.27	0.05	0.022	0.064			307
			14	15	30		41			
1b	99.67	0.002	0.028	0.17	0.054	0.016	0.063			375
			12	37	24		28			
2a	99.65	0.003	0.031	0.23	0.064	0.007	0.018			307
			18	34	37		11			
2b	99.72	0.002	0.037	0.16	0.069	0.011	0.009			375
			20	39	37		5			
Mole Percent of Gas Formed at 60°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
3a	99.53	0.003	0.029	0.31	0.062	0.05	0.02			307
			12	55	25	0.06	8			
3b	99.57	0.003	0.034	0.301	0.05	0.04	0.005			375
			15	60	22		2			
4a	29.6	0.66	0.009	55	0.02	14.8	0.03			307
			27		59		14			
4b	99.69	0.002	0.041	0.17	0.065	0.03	0.008			375
			20	43	32	1.3	4			
Mole Percent of Gas Formed at 75°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
5a	99.39	0.002	0.06	0.33	0.164	0.04	0.02			307
			11	49	32	3	4			
5b	99.4	0.002	0.054	0.25	0.25	0.02	0.02			375
			11	34	51		3			
6a	99.42	0.002	0.06	0.29	0.179	0.03	0.02	0.002		306
			12	43	38	2.2	4	0.4		
6b	99.47		0.06	0.19	0.249	0.02	0.02			375
			11	36	47	3.4	3			
Mole Percent of Gas Formed at 90°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
7a	98.39	0.005	0.09	0.6	0.85	0.03	0.02	0.002	0.003	306
			7.2	22	68.3		2	0.16	0.2	
7b	98.6	0.003	0.071	0.4	0.95	0.01		0.00	0.001	375
			5.7	18	76.2			0.16	0.08	
8a	98.59	0.003	0.10	0.4	0.81	0.044	0.01	0.001	0.003	306
			8.7	22	67.8		1	0.08	0.3	
8b	97.5	0.011	0.088	1.3	0.96	0.163				375
			5.8	31	63.1					
Mole Percent of Gas Formed at 105°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
9a	95.8	0.003	0.24	1.2	2.7	0.04		0.006	0.007	305
			5.9	26	68.0			0.15	0.2	
9b	96.4	0.001	0.17	1.0	2.4	0.03		0.01		375
			4.9	25	69.4	0.1		0.20		
10a	95.6	0.003	0.21	1.2	3	0.037		0.008	0.007	301
			5.0	24	70.7			0.19	0.2	
10b	96.3	0.001	0.15	0.9	2.7	0.022		0.01	0.001	375
			4.0	22	73.7			0.25	0.03	
(a) Blank entries are below detection limits.										



Argon was used to indicate atmospheric contamination because it was not present in the cover gas and was not produced from the waste. Any nitrogen present could have been generated by the waste or come from atmospheric contamination. The percent nitrogen generated is given by the percent nitrogen found minus 83.6 times the percent argon in the sample (the ratio of nitrogen to argon in dry air is 83.6). The uncertainty of approximately 0.001 in argon values translates to an uncertainty of 0.08 in the percent nitrogen produced. The argon-corrected percent nitrogen in the runs at 60°C is only about 50% higher than this value. The rate of oxygen generation cannot be determined by the present experiment because tank material consumes oxygen when it is heated (Person 1996). The uncertainty in the argon values translates to an uncertainty of 0.02 in the percent oxygen produced. The percent oxygen found in the samples was always less than this value and often negative, indicating that it was indeed being consumed.

The mole percent composition for the initial gas samples at each temperature is shown graphically in Figure 9. The percent hydrogen decreased slightly with temperature, and the percent nitrous oxide increased with temperature. Using the percent composition data, reaction times, and mass of each sample, rates of gas generation were determined as a function of temperature and are given in Table 6.

The composition of carbon dioxide (after correction from atmospheric contamination sources) is significant in the low-temperature data and decreases with increasing temperature (Figure 9). High concentrations of carbon dioxide are generally not observed in Hanford tank waste samples studied in the past (Bryan et al. 1996).<sup>(a,b,c)</sup> Presumably, this is because the CO<sub>2</sub> is rapidly absorbed by the high caustic in tank waste; but with the low caustic environment of this experiment, there probably was not enough



**Figure 9.** Percent Composition of Major Gas Products from Thermal Reactions of AN-102 Waste as a Function of Temperature. Error bars give the range of duplicate samples.

(a) Bryan SA and CM King. 1998a. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste: Status Report*. TWS98.39. Pacific Northwest National Laboratory, Richland, WA.

(b) Bryan SA and CM King. 1998b. *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

(c) King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.



**Table 6.** Gas-Generation Rates from Thermal Treatment of Washed AN-102 Material in the Absence of an External Radiation Source. Rates are expressed in moles of gas generated per kg of total sample (wet AN-102 sludge) per day or mol/kg/day.

45°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
1a	9.9E-7	1.0E-6	2.1E-6		2.9E-06			7.0E-6
1b	1.0E-6	3.0E-6	1.9E-6		2.3E-06			8.2E-6
2a	1.4E-6	2.6E-6	2.8E-6		8.0E-07			7.6E-6
2b	1.3E-6	2.5E-6	2.4E-6		3.2E-07			6.6E-6
60°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
3a	1.3E-6	6.4E-6	2.8E-6	6.6E-9	9.6E-07			1.2E-5
3b	1.3E-6	5.0E-6	1.9E-6		1.9E-07			8.3E-6
4a	1.3E-6		2.9E-6		7.1E-07			4.9E-6
4b	1.4E-6	3.1E-6	2.3E-6	9.0E-8	2.8E-07			7.2E-6
75°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
5a	2.6E-6	1.1E-5	7.6E-6	7.2E-7	9.7E-07			2.3E-5
5b	2.0E-6	6.1E-6	9.2E-6		6.3E-07			1.8E-5
6a	2.7E-6	9.8E-6	8.5E-6	5.0E-7	1.0E-06	9.5E-8		2.3E-5
6b	2.3E-6	7.3E-6	9.5E-6	6.9E-7	5.7E-07			2.0E-5
90°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
7a	4.1E-6	1.2E-5	3.8E-5		1.1E-06	9.0E-8	1.4E-7	5.6E-5
7b	2.6E-6	8.2E-6	3.5E-5			7.4E-8	3.7E-8	4.6E-5
8a	4.6E-6	1.2E-5	3.6E-5		6.2E-07	4.4E-8	1.3E-7	5.3E-5
8b	3.1E-6	1.7E-5	3.4E-5					5.3E-5
105°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
9a	1.2E-5	5.4E-5	1.4E-4			3.2E-7	3.7E-7	2.1E-4
9b	7.0E-6	3.7E-5	1.0E-4	1.5E-7		2.9E-7		1.4E-4
10a	1.0E-5	5.0E-5	1.5E-4			3.9E-7	3.4E-7	2.1E-4
10b	5.8E-6	3.2E-5	1.1E-4			3.5E-7	3.9E-8	1.4E-4

caustic to do the job. The rate of carbon dioxide generation is observed to decrease with increasing temperature. All other gases generated in the AN-102 washed sludge sample are observed to increase the generation rate with increasing temperature. The reason for a decrease in carbon dioxide generation is not understood.

### 3.1.2 Radiolytic Gas Generation from Tank AN-102 Waste

This section contains the data from enhancing radiolytic gas generation by placing a <sup>137</sup>Cs source (gamma capsule) next to the reaction vessels while heating the material in the reaction vessels to temperatures of 45°, 60°, 75°, 90°, and 105°C. Two gas samples were taken from each of the 10 reaction vessels. The mole percent composition of the gas sampled at the end of each run is given in Table 7. The rates of gas generation from each run are given in Table 8.

**Table 7.** Mole Percent Composition of Radiolytic Gas Sampled (including Ne) and Formed (shaded), and Heating Times of Duplicate Systems at Five Temperatures (external radiation source)<sup>(a)</sup>

Mole Percent of Gas Formed at 45°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
11a	34.5	0.61	0.176	51.0	0.229	13.4	0.009	0.002		162
			26.2	41.6	34.0			0.3		
11b	97.8	0.002	0.56	0.75	0.84	0.018		0.01		162
			27.0	32.2	40.6			0.2		
12a	98.7	0.002	0.314	0.49	0.45	0.036		0.00		162
			26	34.2	37.9	1.1		0.3		
12b	97.6	0.004	0.53	1.1	0.72	0.025		0.01		162
			25.2	40.4	34.2			0.2		
Mole Percent of Gas Formed at 60°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
13a	98.7	0.003	0.30	0.5	0.52	0.03		0.004		161
			26.1	27.6	45.9			0.4		
13b	97.8	0.002	0.53	0.83	0.82	0.025		0.01		162
			25.2	35.5	39.0	0.1		0.3		
14a	98.2	0.003	0.47	0.61	0.66	0.027		0.01		161
			30	28.0	41.8			0.3		
14b	97.7	0.001	0.60	0.76	0.91	0.013		0.01		162
			27.4	30.9	41.5			0.3		
Mole Percent of Gas Formed at 75°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
15a	98.3	0.002	0.43	0.5	0.660	0.03		0.004		161
			27.7	29.4	42.5	0.2		0.3		
15b	98.2	0.001	0.47	0.49	0.82	0.015		0.004		162
			27.6	23.9	48.2			0.2		
16a	98.3	0.001	0.44	0.448	0.74	0.02		0.00		161
			29	23.5	47.7			0.3		
16b	97.9	0.001	0.59	0.51	0.98	0.006		0.01		162
			29.5	21.3	49.0			0.2		
Mole Percent of Gas Formed at 90°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
17a	97.2	0.002	0.74	0.9	1.05	0.02		0.009	0.004	161
			27.8	32.2	39.5			0.3	0.150	
17b	97.5	0.001	0.73	0.8	0.98	0.017		0.01	0.006	162
			29.9	29.3	40.1			0.4	0.246	
18a	96.2	0.018	0.48	2.19	0.69	0.4		0.01		161
			24	39.2	35.1	1.0		0.3		
18b	96.5	0.018	0.37	2.02	0.73	0.319		0.01	0.002	162
			21.6	35.2	42.9			0.3	0.1	
Mole Percent of Gas Formed at 105°C										
Run	Ne	Ar	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Time, h
19a	97.6		0.73	0.7	0.95	0.0		0.008	0.002	161
			30.3	29.5	39.4	0.4		0.3	0.083	
19b	97.2		0.87	0.67	1.21	0.008		0.01	0.010	162
			31.3	24.1	43.5	0.3		0.4	0.360	
20a	97	0.003	0.86	0.94	1.15	0.047		0.01	0.005	161
			31	27.6	41.1	0.08		0.3	0.179	
20b	96.2		1.31	0.94	1.55	0.01		0.02	0.012	162
			34.1	24.5	40.4	0.3		0.4	0.3	
(a) Blank entries are below detection limits.										

**Table 8.** Gas-Generation Rates from Radiolytic Treatment of Tank AN-102 Material in the Presence of an External Radiation Source. Rates are expressed in moles gas generated per kg of total sample (wet AN-102 sludge) per day; or mol/kg/day.

45°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
11a	4.2E-5	6.6E-5	5.4E-5			4.4E-7		1.6E-4
11b	4.7E-5	5.6E-5	7.1E-5			4.2E-7		1.7E-4
12a	2.9E-5	3.7E-5	4.1E-5	1.2E-6		2.7E-7		1.1E-4
12b	4.8E-5	7.7E-5	6.5E-5			4.5E-7		1.9E-4
60°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
13a	2.7E-5	2.8E-5	4.7E-5			3.6E-7		1.0E-4
13b	4.7E-5	6.6E-5	7.3E-5	2.3E-7		5.3E-7		1.9E-4
14a	4.3E-5	4.0E-5	6.0E-5			4.5E-7		1.4E-4
14b	5.4E-5	6.1E-5	8.1E-5			5.4E-7		2.0E-4
75°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
15a	4.0E-5	4.3E-5	6.2E-5	2.4E-7		3.7E-7		1.5E-4
15b	4.3E-5	3.8E-5	7.6E-5			3.7E-7		1.6E-4
16a	4.1E-5	3.3E-5	6.8E-5			3.7E-7		1.4E-4
16b	5.4E-5	3.9E-5	8.9E-5			4.5E-7		1.8E-4
90°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
17a	6.6E-5	7.6E-5	9.3E-5			8.0E-7	3.6E-7	2.4E-4
17b	6.4E-5	6.3E-5	8.6E-5			7.9E-7	5.3E-7	2.1E-4
18a	4.3E-5	6.9E-5	6.2E-5	1.7E-6		5.4E-7		1.8E-4
18b	3.3E-5	5.3E-5	6.5E-5			4.5E-7	1.8E-7	1.5E-4
105°C Gas-Generation Rates, mol/kg/day								
Run	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	other hydrocarbons	Total
19a	7.3E-5	7.1E-5	9.5E-5	9.0E-7		8.0E-7	2.0E-7	2.4E-4
19b	8.5E-5	6.6E-5	1.2E-4	7.9E-7		1.1E-6	9.8E-7	2.7E-4
20a	8.0E-5	7.2E-5	1.1E-4	2.0E-7		7.4E-7	4.6E-7	2.6E-4
20b	1.2E-4	8.6E-5	1.4E-4	9.1E-7		1.4E-6	1.1E-6	3.5E-4

### 3.2 Thermal and Radiolytic Rate Parameters for Gas Generation from Tank AN-102 Waste

The three most important mechanisms for gas generation from wastes contained in Hanford tanks have been determined to be 1) radiolytic decomposition of water and some organic species; 2) thermally driven chemical reactions, mainly involving organic complexants, solvents, and other solution species; and 3) chemical decomposition of the steel tank walls (Johnson et al. 1997). The total gas-generation rate is the sum of the radiolytic, thermal, and corrosion rates:

$$\text{Total Rate} = \text{Radiolytic Rate} + \text{Thermal Rate} + \text{Corrosion Rate} \quad (3.1)$$

Because radiolytic and thermal rates dominate (Johnson et al. 1997), they are the focus of these experiments.

The thermal rate varies with temperature. The relation between thermal rate constant,  $k$ , at different temperatures is given by the Arrhenius equation:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (3.2)$$

where  $R$  is the gas constant, 8.314 J/K-mol,  $T$  is the temperature in Kelvin,  $E_a$  is the activation energy, and  $A$  is the pre-exponential factor. The initial thermal rate is assumed to be zero-order (Espenson 1981), in which case the rate constant is equivalent to the observed rate. Values of  $E_a$  and  $A$  can then be determined from the rates measured in the reaction vessels. The equation allows the thermal rates to be calculated at temperatures where the rate is so slow it is difficult to measure directly.

The radiolytic rate at a given temperature is determined experimentally by measuring the difference between rates measured in the presence and absence of external radiation. The G-value, a dose-independent rate, is related to the radiolytic rate by equation 3:

$$\text{G-value(molecules/100 eV)} = \frac{\text{Radiolytic rate (mol/kg/day)}}{\text{Dose rate (R/hr)}} \times (4.02 \times 10^7) \quad (3.3)$$

The constant  $4.02 \times 10^7$  is a unit conversion factor. The 95% confidence interval for the thermal rates is obtained from the thermal data. The 95% confidence interval rates measured in the presence of external radiation are estimated at given temperatures as half the range of the duplicate measurements. Radiolytic rates have been observed to be essentially temperature-independent over the temperature range studied both in water radiolysis (Draganic and Draganic 1971) and in the radiolytic rates measured in Hanford waste tank material.<sup>(a,b,c)</sup>

The activation energy for the initial rate of gas formation for each thermal gas reaction system was estimated from gas composition and generation data for sample "a" from each run (approximately the initial 300-hour reaction time) (Tables 6 and 8). A plot of the total gas generated is shown in Figure 10. This figure shows the total gas generated from washed AN-102 waste under self radiolysis and high dose conditions. The calculated fits of the data use thermal activation energies ( $E_a$ ) and G-values from Table 9. The activation energy for total gas formation was found to be  $109 (\pm 40)$  kJ/mole (95% confidence level).

Generation rates of the major gas components from washed AN-102 waste under self-radiolysis conditions are shown in Figure 11. Based on the formation rate of each gas component in the reaction vessel, thermal Arrhenius activation parameters and radiolytic G-values can be calculated for the major components. The gas-generation rate data for self-radiolytic generation at various temperatures for  $H_2$ ,  $N_2O$ ,  $N_2$ , and  $CH_4$  are shown in Figure 11. The fits of the data use thermal activation energies ( $E_a$ ) and G-values from Table 9. The activation energies ( $E_a$ ) for formation of these components are  $63(\pm 16)$  kJ/mole (95% confidence interval) for  $H_2$ ,  $111(\pm 28)$  kJ/mole for  $N_2O$ ,  $58(\pm 29)$  kJ/mole for  $N_2$ , and  $71(\pm 155)$  for  $CH_4$ .

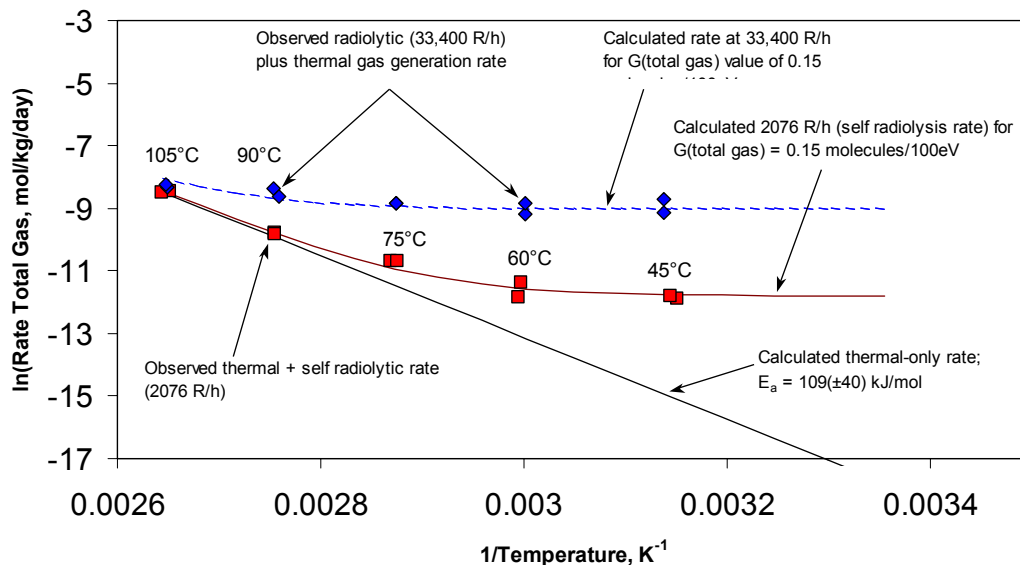
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(a) Bryan SA and CM King. 1998a. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste: Status Report*. TWS98.39. Pacific Northwest National Laboratory, Richland, WA.

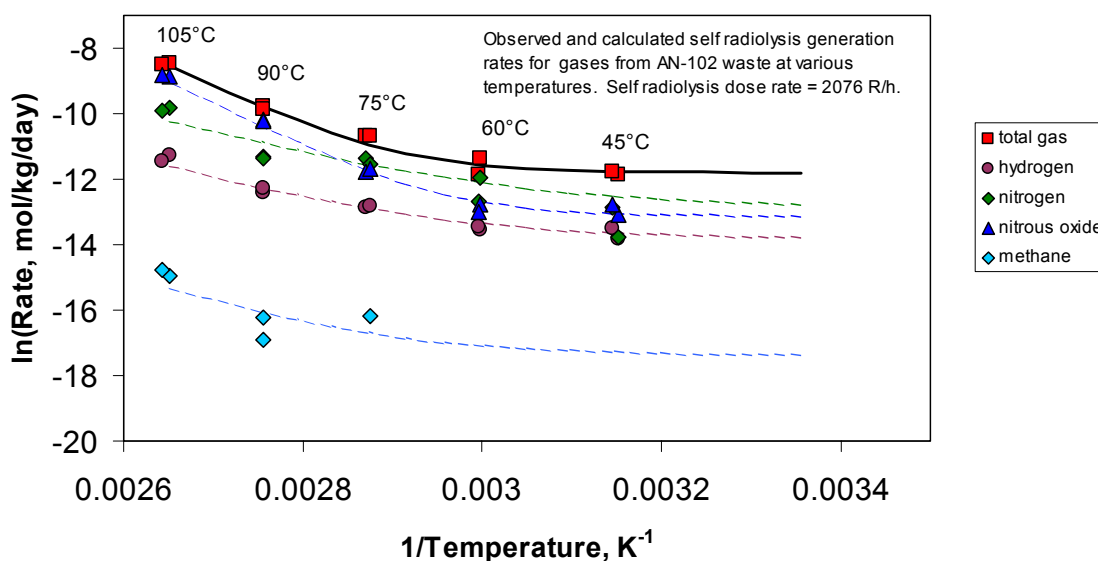
(b) Bryan SA and CM King. 1998b. *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

(c) King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

The experimental thermal and radiolytic rates for duplicate runs for hydrogen, nitrous oxide, nitrogen, and methane generation, represented by symbols, are shown in Figure 12. The curved lines in the figure are predicted temperature-independent radiolytic rates, which are thermal rates plus a constant representing a G-value. The G-values derived from these data are listed in Table 9.



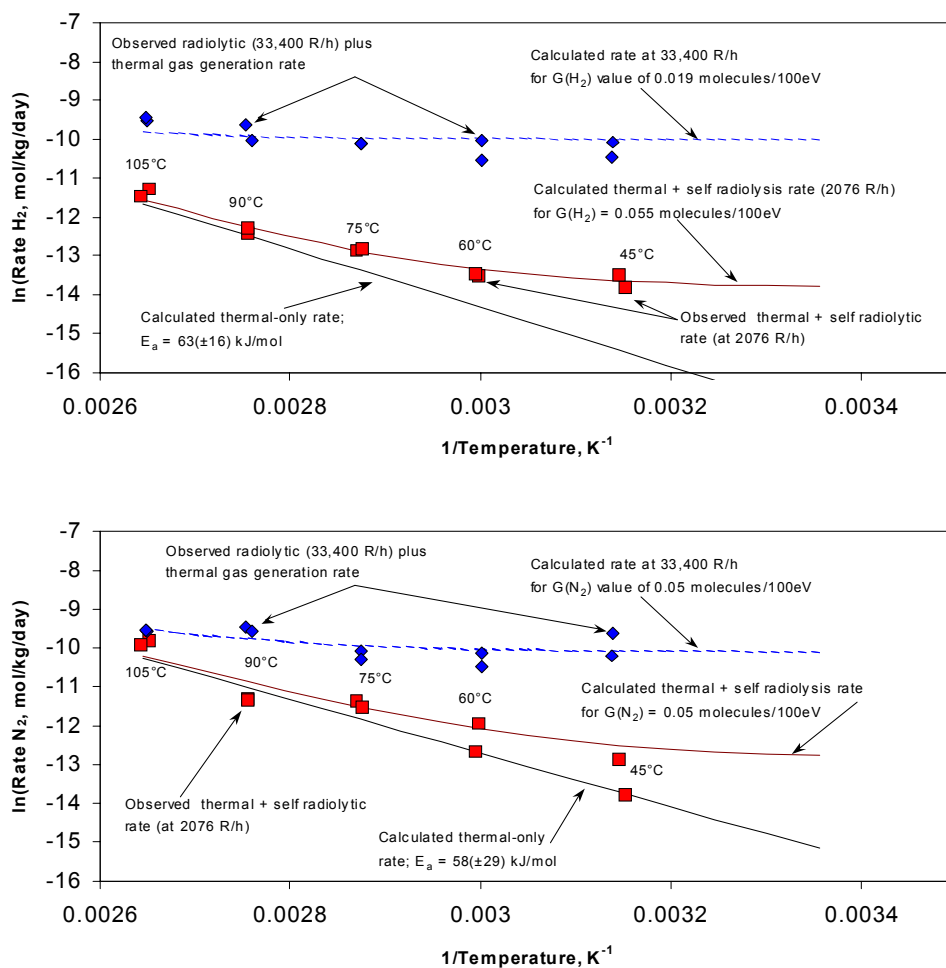
**Figure 10.** Rates of Total Gas Generated from Washed AN-102 Waste under Self-Radiolysis and High-Dose Conditions. Calculated fits of the data use thermal activation energy ( $E_a$ ) and G-values from Table 9.



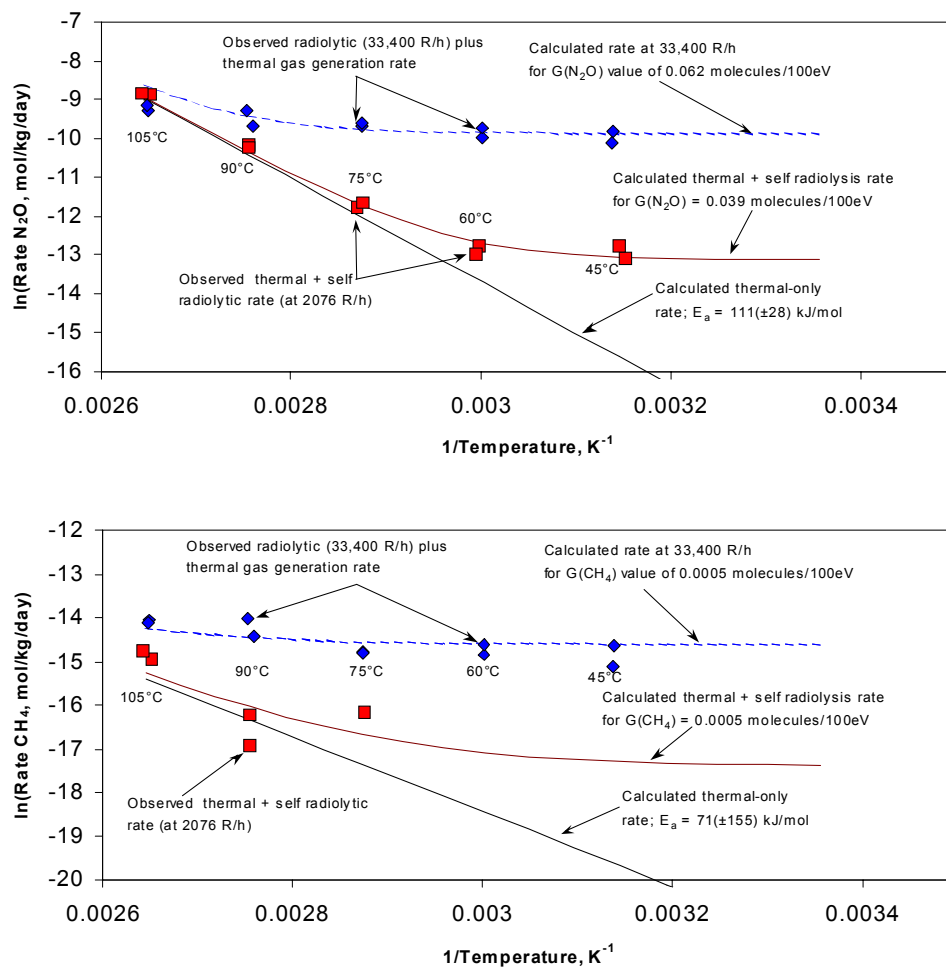
**Figure 11.** Formation of Major Gas Components from Washed AN-102 Waste under Self-Radiolysis Conditions. Calculated data fits use thermal activation energies and G-values from Table 9.

**Table 9.** Thermal and Radiolytic Rate Parameters for Gas Generation from Washed AN-102 Waste

	H <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub>	CH <sub>4</sub>	Overall rate
E <sub>a</sub> , kJ/mol	63(±16)	111(±28)	58(±29)	71(±155)	109(±40)
A, mol/kg/day	3.81E+03	2.75E+11	3.30E+03	1.38E+03	2.09E+11
ln(A)	8(±5)	26(±10)	8(±10)	7(±51)	26(±14)
R <sup>2</sup>	0.928	0.915	0.835	0.415	0.856
G-value at 33,400 R/h	0.055 (±0.018)	0.062 (±0.013)	0.0495 (±0.016)	0.0005 (±0.0002)	0.145 (±0.051)
G-Value at 2076 R/h	0.019 (±0.007)	0.039 (±0.013)	0.0495 (±0.016)	0.0005 (±0.0002)	0.145 (±0.051)



**Figure 12a.** Tank AN-102 Thermal and Radiolytic Gas-Generation Rates for Hydrogen and Nitrogen



**Figure 12b.** Tank AN-102 Thermal and Radiolytic Gas-Generation Rates for Nitrous Oxide and Methane

## 4.0 Energetics of AN-102 Washed Solids

During processing of AN-102 wastes, the solids will be filtered and washed via ultrafiltration and accumulated in a tank in the pretreatment area of the HLW vitrification plant. Because AN-102 wastes contain significant concentrations of organics and inorganic oxidants and at least one sample exhibited significant energetics, CH2M HILL Hanford Group requested that PNWD measure the energetics of washed AN-102 solids to help assess the washed solids' reactivity hazard.<sup>(a)</sup>

The potential reactivity of Hanford HLW has been a concern because several of the stored wastes contain fuels (organic compounds) and oxidants (nitrates and nitrites) whose reactions are thermally sensitive (Scheele et al. 1995; Wahl et al. 1996; Meacham et al. 1997). Because of this concern, Hanford laboratories screened thousands of waste samples using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to determine whether their thermally induced energetics exceeded 480 J/g dry waste (Babad et al. 1995). If their DSC-measured energetics exceeded this criterion, they further characterized the waste using the Reactive System Screening Tool (RSST). Meacham et al. (1997) concluded that the wastes stored in Hanford's single-shell tanks posed no reactivity risks.

Unwashed AN-102 wastes contain up to 30 g total organic carbon (TOC) per liter of solids combined with the inorganic oxidants nitrates and nitrites. These wastes have been found to exhibit significant exothermicity (488 J/g dry waste) (TWINS3 database). Thus, depending on the behavior of the organic compounds and nitrate/nitrite during washing, washed AN-102 solids could exhibit significant energetics, which is a concern (Reynolds 2001).

In support of the Hanford HLW vitrification plant project, we followed the strategy of Babad et al. (1995) using TGA and differential thermal analysis (DTA), which is similar to DSC, to determine the washed AN-102 solids energetics. The results of our work are described in this section.

### 4.1 Composition of Washed AN-102 Solids

The AN-102 washed solids used for this energetics testing were prepared as described in Section 2.2. Table 10 provides the measured composition of the washed AN-102 solids. Based on this analysis, the solids were 52.5% water.

The only organic compound observed in the AN-102 washed solids is oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) at 1.3 mmol/g or 2.6 mmol C/g. Sodium oxalate has less energetics than other organic compounds (Meacham et al. 1997; Wahl et al. 1996; Burger 1995). After washing, the soluble oxidants nitrate and nitrite were present in the solids at 0.7 and 0.4 mmol/g, respectively. The molar stoichiometric ratios for the maximum enthalpy-producing reactions between oxalate and nitrate or nitrite are 1:0.4 and 1:0.67, respectively (Burger 1995). There are nearly stoichiometric amounts (slight deficiency) of each individual oxidant in the solids; together there are sufficient nitrate and nitrite for full reaction via the most energetic reaction path. The maximum amount of heat theoretically produced by a reaction between 2.6 wt% C as oxalate

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(a) Reynolds DE. 2001. Test Specification: *Energetics and Gas Generation Studies*. TSP-W375-01-00002, CH2M HILL Hanford Group, Inc., Richland, WA.



**Table 10.** Measured Composition of AN-102 Washed Solids

Waste Constituent	Concentration, wt %	Concentration, mmol/g
F <sup>-</sup>	0.17	0.89
Cl <sup>-</sup>	0.07	0.021
NO <sub>2</sub> <sup>-</sup>	1.79	0.39
NO <sub>3</sub> <sup>-</sup>	4.08	0.66
PO <sub>4</sub> <sup>3-</sup>	0.28	0.029
SO <sub>4</sub> <sup>2-</sup>	0.49	0.051
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	8.92	1.0
OH <sup>-</sup>	0.55	0.32
Total Organic C (TOC)	2.5	2.1
Al	13.1	4.9
Na	16.3	7.1
Cr	0.96	0.19
Fe	0.66	0.18
Mn	0.15	0.027
H <sub>2</sub> O	52.5	

and sodium nitrate or nitrite and hydroxide is 320 J/g mix or 580 J/g dry waste based on Burger's (1995) reported reaction enthalpies. Because of their oxalate and nitrate/nitrite concentrations, the washed AN-102 solids could theoretically produce >480 J/g of dry waste.

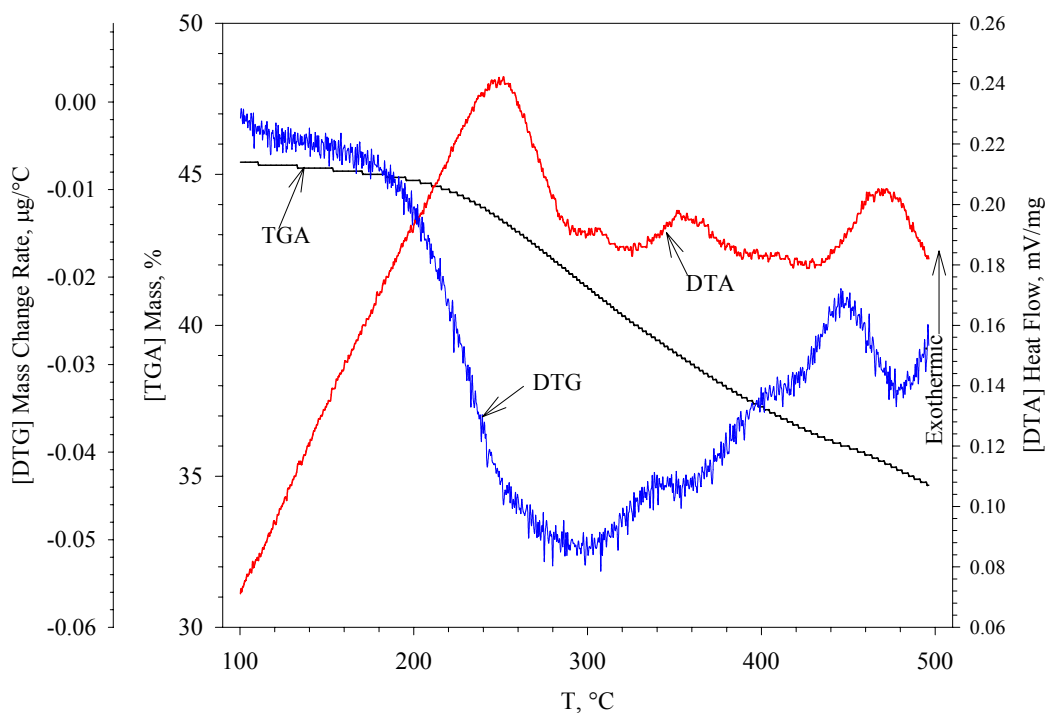
## 4.2 Measurement Strategy

Just as Hanford used the Babad et al. (1995) strategy to assess the reactivity hazards of stored organic-bearing HLW (Meacham et al. 1997), at the direction of CH2M HILL (Reynolds 2001), we used the same basic strategy using enthalpy-calibrated DTA rather than DSC from room temperature to 500°C. We calibrated the DTA using known melting point standards. In the event that we saw an exothermic reaction producing >480 J/g dry waste, we were to analyze the material using the RSST after concurrence of Bechtel National Inc. Scheele et al. (1995), Wahl et al. (1996), and CCPS (1995) contain descriptions of the thermoanalytical methods.

To measure heat changes in the AN-102 sample, we programmed the DTA/TGA instrument to heat to 100°C at 5°C/min, hold at 100°C for 30 minutes to evaporate any free water, and then heat to 500°C at 5°C/min. We used argon as the purge gas to eliminate oxygen and any of its reactions with organics in the waste during the analysis. We did the analyses in triplicate.

## 4.3 Results

The AN-102 washed solids exhibited exothermic behavior, as shown in Figure 13, which presents the average of the triplicate DTA, TGA, and differential thermogravimetric (DTG) analyses for the washed AN-102 solids between 100 and 500°C. The sample was held at 100°C for 30 minutes to dry before continuing the thermal analysis.



**Figure 13.** Average Thermal Behavior of Washed AN-102 Solids from 100° to 500°C

The drying reaction is not presented in Figure 13 to facilitate analysis of the reactions between oxalate and nitrate or nitrite. The DTG is the derivative of the TGA and is another tool favored to help identify where reactions begin and end. The DTG has an appearance similar to the DTA or DSC curve. As shown in the figure, the original samples contained an average of 46 wt% solids (54 wt% water) based on the samples' mass after heating at 100°C for 30 minutes. This is consistent with the analytical value of 52.5% H<sub>2</sub>O listed in Table 10. There are essentially three heat-producing events using TGA as a guide for start and end temperatures. These are summarized in Table 11. Exothermic enthalpies are indicated by a negative sign and endothermic by a positive sign.

The first reaction, after water loss below 100°C, occurs between 200° and 327°C. Based on the DTG, it produced about 40 J/g waste with an average 4.8 wt% loss. The second reaction occurs between 327° and 400°C and produces about 4.7 J/g with a 2 wt% loss. The third reaction occurs between 440° and 500°C and produces 10 J/g with a mass loss of 1.4 wt%. The average total heat produced between 100° and 500°C is 55 J/g washed solids or 110 J/g dry AN-102 solids, or well below the 480 J/g dry waste criterion required for a waste to be designated as a potential reaction hazard. Because the heat released is less than the criterion, we performed no RSST analyses.

The only organic in the AN-102 washed solids was oxalate. Mixtures of oxalate and nitrate/nitrite are reactive (Wahl et. al. 1996); however, the amount of heat produced depends on the oxalate concentration. Using Burger's (1995) calculated reaction enthalpies, a 2.4 wt% C-as-oxalate mixture of sodium oxalate and a stoichiometric amount of sodium nitrate can theoretically produce a maximum of 170 J/g mix. The maximum amount heat theoretically produced by a reaction between 2.4 wt% C as oxalate and sodium nitrite is 217 J/g mix. Hydroxide participation increases the maximum theoretical enthalpy

**Table 11.** Thermal Behavior of AN-102 as Measured by DTA/TGA

<b>Sample</b>	<b>Event Temperature Range (°C)</b>	<b>Mass Loss (wt%)</b>	<b>Enthalpy Change (J/g)</b>
Analysis #1	20-100	58	1010
	200-327	4.5	-41
	327-400	2.4	-7
	440-500	1.3	-6
	Total (100-500°C)	9.3	-54
Analysis #2	20-100	53	440
	200-327	5.0	-37
	327-400	1.7	-4
	440-500	1.5	-14
	Total (100-500°C)	10.3	-55
Analysis #3	20-100	52	600
	200-327	5.0	-39
	327-400	1.9	-3
	440-500	1.4	-12
	Total (100-500°C)	10.5	-54
Average	20-100	54	680
	200-327	4.8	-39
	327-400	2.0	-5
	440-500	1.4	-11
	Total (100-500°C)	10.0	-54

changes for oxalate's reaction with nitrate and nitrite by 60 and 39%, respectively. Based on the oxalate concentration and TOC, the maximum heat that could be produced by the washed AN-102 waste is 300 J/g or 650 J/g dry waste, assuming reaction with nitrite and hydroxide.

The heat measured is less than any theoretical maximum. The measured 55 J/g waste is 20% of the maximum theoretical for oxalate's reaction with nitrate and hydroxide or 18% of the maximum theoretical for the reaction between oxalate and nitrite and hydroxide. These results are consistent with studies of oxalate reactions with nitrate and/or nitrite. Scheele found that, for a 6 wt% TOC oxalate-nitrate mixture, the DSC observed 5% and the DTA observed 20% of the maximum theoretical heat (Wahl et. al. 1996). For the oxalate-nitrite mixture, Scheele measured 18 and 45% of the theoretical maximum using the DSC and DTA, respectively. We believe that the difference between the measured and theoretical maximum heat releases can be explained by 1) the oxidation proceeding via a different pathway (calculated values not properly descriptive of the reaction chemistry) or 2) the gas products carry away much of the heat produced without the heat being observed by the DSC and DTA (a less accurate experimental method). We have no explanation for the differences between DTA and DSC.

In summary, the AN-102 washed solids exhibited exothermic behavior; however, the heat released fell below the Hanford threshold criteria of a DSC-measured 480 J/g dry waste (Babad et al. 1995) used to identify reactive wastes. Because these washed solids fell below this threshold, we did not attempt to measure the enthalpy using the RSST. The heat measured was substantially less than the theoretical maximum expected for the reaction of nitrate and nitrite salts with oxalate present in the tank waste.

## 5.0 Summary and Conclusions

This report summarizes progress made in evaluating mechanisms by which flammable gases are generated in washed sludge from Hanford Tank 241-AN-102. Gas generation from AN-102 sludge samples was first measured with externally applied heat, then with externally applied heat and radiation ( $^{137}\text{Cs}$  capsule).

The objective of this work was to establish the composition of gaseous degradation products formed in actual tank sludges by thermal and radiolytic processes as a function of temperature. The focus of the gas-generation tests on Tank AN-102 samples was first on the effect of temperature on the composition and rate of gas generation. Generation rates of hydrogen, nitrous oxide, nitrogen, and methane increased with temperature, and the composition of the product gas mixture varied with temperature. The gas-generation rate was examined at 45°, 60°, 75°, 90°, and 105°C. Arrhenius treatment of the rate data yielded activation parameters for gas generation. The measured thermal activation energies,  $E_a$ , were determined to be 63 ( $\pm 16$ ) kJ/mole for  $\text{H}_2$ , 111 ( $\pm 28$ ) kJ/mole for  $\text{N}_2\text{O}$ , 58 ( $\pm 29$ ) kJ/mole for  $\text{N}_2$ , and 71 ( $\pm 155$ ) for  $\text{CH}_4$ .

The gas generation in the presence of a 31,300 R/hr ( $^{137}\text{Cs}$ ) external gamma source was performed to measure the radiolytic G-values for gas generation. The effect of radiation was examined at 45°, 60°, 75°, 90°, and 105°C. The radiolytic G-values, in molecules per 100 eV, were determined to be 0.055 ( $\pm 0.018$ ) for hydrogen, 0.062 ( $\pm 0.013$ ) for nitrous oxide, 0.0495 ( $\pm 0.016$ ) for nitrogen, and 0.0005 ( $\pm 0.0002$ ) for methane.

The AN-102 washed solids exhibited exothermic behavior; however, the heat released fell below the Hanford threshold criterion of a DSC-measured 480 J/g dry waste (Babad et al. 1995) used to identify reactive wastes. Because these washed solids fell below this threshold criterion, we did not attempt to measure the enthalpy using the RSST. The heat measured was substantially less than the theoretical maximum expected for the reaction of nitrate and nitrite salts with oxalate present in the tank waste.

Analytical reports detailing analytic measurements of the washed AN-102 waste used in this study are summarized in the appendixes to this report.



## 6.0 References

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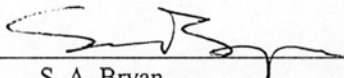
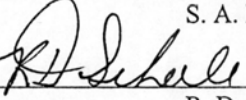
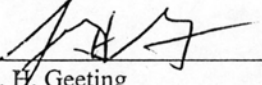
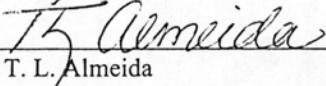
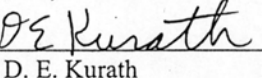
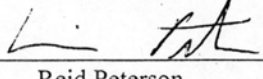
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## **Appendix A**

### **Battelle Test Plan TP-RPP-WTP-066: *Energetics and Gas Generation***



*copy*

<b>Battelle Test Plan</b>		Document No.: TP-RPP-WTP-066 Rev. No.: 0
Title: Energetics and Gas Generation Tests		
Work Location: RPL/Various	Page 1 of 9	
Author: S.A. Bryan/R. D. Scheele	Effective Date: March 2001 Supersedes Date: New	
<b>Identified Hazards:</b> <input checked="" type="checkbox"/> Radiological <input checked="" type="checkbox"/> Hazardous Materials <input checked="" type="checkbox"/> Physical Hazards <input type="checkbox"/> Hazardous Environment <input type="checkbox"/> Other:	<b>Required Reviewers:</b> <input checked="" type="checkbox"/> Author <input checked="" type="checkbox"/> Technical Reviewer <input checked="" type="checkbox"/> Quality Engineer <input checked="" type="checkbox"/> Project Manager <input checked="" type="checkbox"/> Client	
<b>Approval</b>	<b>Signature</b>	<b>Date</b>
Author	 S. A. Bryan	5/1/01
Author	 R. D. Scheele	5/1/01
Technical Reviewer	 J. G. H. Geeting	5-1-01
Quality Engineer	 T. L. Almeida	5/2/01
Project Manager	 D. E. Kurath	5/1/01
Client	 Reid Peterson	5/16/01

**Applicability**

This test plan applies to the:

- 1) Washing of Tank 241-AN-102 waste materials for use in this task.
- 2) Gas generation measurements on heat treated and irradiated, washed Tank 241-AN-102 waste materials, and Sr/TRU precipitated AN-102 solids (if quantity of solids permits).
- 3) Screening of the washed AN-102 high level waste (HLW) solids and Sr/TRU precipitated solids using a differential scanning calorimeter (DSC) or differential thermal analyzer (DTA) to determine if there are energetic exothermic reactions.
- 4) Determination of water content in the washed AN-102 high level waste (HLW) solids using thermogravimetric analysis (TGA).
- 5) Supplemental measurement of exothermic behavior, using the Reactive System Screening Tool (RSST) and a larger sample, if the DSC- or DTA-measured exotherm(s) are greater than 480 J/g dry waste. The RSST provides additional data including an improved measure of exothermic energetics and thermal behavior.

Irradiation of the Hanford tank waste materials and collection of the gases will be performed within PNNL's High Level Radiation Facility (HLRF) in the Radiochemical Processing Laboratory (RPL). The other activities will be performed in various laboratories in the RPL. This test plan applies to staff working on these activities at PNNL's Gamma Irradiation Facility (GIF) and in the RPL and includes laboratory technicians, scientists and engineers.

**DRD and Other References**

Test specifications for this activity were provided by CH2M Hill Hanford Group, Inc. (CHG) in document TSP-W375-01-00002, Rev. 0, "Energetics and Gas Generation Studies", (DA Reynolds and M.E. Johnson, 2/27/01).

**Definitions**

None.

**Justification**

This activity provides information on gas generation capacity and reactivity of Tank 241-AN-102 waste material. The energetic tests evaluates potential for runaway reactions, the gas generation studies explore the rate gases will be generated under thermal and radiolytic conditions. These tests will assist in understanding certain process safety concerns and provide information on potential emissions to the pretreatment vessel off-gas ventilation system.

**Test Objectives**

The RPP-WTP is evaluating gas generation rates and potential for exothermic reaction of the washed solids from Hanford Tank 241-AN-102 to provide information for assessing safe storage conditions. The objectives are:

- Prepare washed solids from Tank 241-AN-102 suitable for use within this task.

- Perform thermal and radiolytic experiments on washed solids from Hanford Tank 241-AN-102 under the following conditions.
  - Thermal treatments at 5 temperatures (in duplicate);
  - Irradiation treatments at same temperatures as thermal treatment (in duplicate);
  - Measure gases evolved during thermal and radiolytic treatments;
  - Determine thermal and radiolytic activation parameters for gas generation
 Also perform identical testing on Sr/TRU precipitated AN-102 solids if the quantity of solids allows.
- Screen the washed AN-102 HLW solids and AN-102 Sr/TRU precipitated solids using a DSC or DTA to determine if there are exothermic reactions. If the DSC- or DTA-measured exotherms are greater than 480 J/g dry waste, then;
- The RSST apparatus will be used with a much larger sample to better quantify the exotherm and provide additional data.

Hanford wastes are known to produce gases and have shown exothermic behavior under certain situations. Hydrogen gas generation will be measured for washed sludge to simulate conditions found in the HLW melter feed tank. The energetics testing outlined in this test specification will provide semi-quantitative measures of the thermally induced exotherms encountered within these wastes.

#### Success Criteria

The RPP-WTP will consider this test successful when the gas composition and gas generation rates versus thermal and radiation exposure are accurately determined for the washed Hanford AN-102 waste. The gas generation and energetics data as measured will provide information for safe storage.

#### Background

The product of the ultrafilter is a solids-bearing stream. This stream will be accumulated in a tank in the pretreatment area of the plant. The solids have the potential for gas generation and for energetic reactions.

Energetics of the waste has been a concern. The waste contains fuel (organics molecules) and oxidizers (nitrate and nitrite ions). The potential for an organic/nitrate reaction has been studied extensively in the tank farm. The conclusion is that an energetic reaction in the waste storage mode in the tank farms is not credible (Meacham et. al. 1997). This is based on thousands of samples from the tanks that were screened using a DSC/TGA method (Babad et. al. 1995). Those wastes that exhibited an exothermic reaction greater than 480 J/g dry waste were further tested with the RSST to identify propagating reactions. No propagating reactions were found. It should be noted that AN-102 was tested a number of times (TWINS3 Database). The highest DSC-measured energetics on a solid sample was 488 J/g on a dry weight basis.

The solid waste stored in the Pretreatment Plant will be washed in the ultrafiltration step. This should remove nearly all of the organics species from the solids. The only organic shown to be in the solid form is sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$  which has been shown to have reduced reactivity compared to other organic compounds. Also the washing should remove nearly all of the oxidizer (nitrate/nitrite). This should leave the solids in a less reactive mode than when in Hanford's HLW storage tanks. Mixtures of oxalate and nitrate/nitrite are reactive, however the amount of heat produced depends on the oxalate concentration. Theoretically a 6 wt% carbon mixture of sodium oxalate and sodium nitrate can produce a maximum of 420 J/g mix, however, PNNL measurements by DSC and DTA have observed reaction heats of 5 and 20% of maximum theoretical (Wahl et. al. 1995).

This test specification is to determine the reactivity of the washed solids. The approach will be a graded approach. The first step will be to test the material using a DSC and/or DTA/TGA. This step uses little waste. If the DSC or DTA shows that the sample may have greater than 480 J/g dry waste, then the larger more complicated RSST test will be performed upon approval.

There have been a number of tests on actual wastes for gas generation done at PNNL (Bryan et al 1996; Bryan and King 1998a, 1998b; King and Bryan 1998; King et al 1999). These tests were used with other information to derive an estimate of the generation rate of gas (Pederson and Bryan 1996; Hu 2000). It is recognized that radiation will produce gas from the radiolysis of water. The washed sludge that is stored in the Pretreatment facility will have most of the organic compounds washed out. The lower organic content should greatly diminish the amount and rate of gas generation of the sludge. However, the reduced nitrate and nitrite content – which when present, acts as a scavenger for hydrogen generation – may have the affect of increasing the gas generation capacity. The tests will determine the gas generation capacity of the low organic wastes with relatively high radiation doses.

### **Description of Tests**

Hanford waste samples from Tank 241-AN-102 have been received, composited, and prepared for use by this task under “Washed BNFL Ultrafiltration Physical Testing: Feed Characterization” task (Paul Bredt, BNFL-TP-41500-015).

The sludge washing will be performed by adding approximately equal volumes of 0.01 *M* NaOH solution with the solids, mixing for 1 hour, followed by a settle-decant. The washing will be repeated three times. The washed solids will be the starting mixture for the gas generation and energetics studies. The washing will simulate the washing that the solids will receive in the pretreatment plant. It is expected that this washing step will remove organics that promote gas generation. However, it is expected to remove nitrate ion that protects against radiolysis of water.

Two samples of the solids prepared in the previous step will be analyzed for: sodium, aluminum, TOC, nitrate, nitrite, hydroxide, and oxalate. Rad-chem analysis will also be performed for the flowing constituents:  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$ , and  $^{244}\text{Cm}$ .

### *Energetics*

PNNL will measure the exothermic reaction potential of wet, washed AN-102 solids and AN-102 Sr/TRU precipitated solids (if quantity of solids permits) using DSC or DTA/TGA. The samples will be analyzed by DSC or DTA/TGA at least in duplicate. For any observed exotherm, its enthalpy will be calculated. If the exotherm(s) are less than 350 J/g wet waste, no further analyses. If the exotherm(s) are greater than 350 J/g wet waste, the water content will be measured using TGA if not already measured. If the DSC- or DTA-measured exothermic enthalpy exceeds 480 J/g dry waste, RPP-WST will be consulted for guidance on the decisions on what material will be analyzed by RSST in a single analysis. Results of the thermal analyses will be reported.

### *Gas Generation Testing*

The effects of temperature and radiation on gas generation from washed Tank 241-AN-102 entrained solids material will be assessed. Gas generation testing of Sr/TRU precipitated solids will also be performed if the quantity of solids is sufficient (~600 g). For AN-102 tank waste, material will come from a composite core samples taken from AN-102. Gas will be generated at five temperatures: 60, 75, 90, 105, and 120°C, in the presence and absence of external gamma radiation (supplied by a  $^{137}\text{Cs}$



capsule), for a total of 10 experimental variations. Each experiment will be performed in duplicate, giving a total of 20 experiments. Each reaction will use approximately 20-30 g of tank material. A total of approximately 600g of washed Tank 241-AN-102 material will be required for testing. The rate of gas generation in the presence of external radiation is the sum of radiolytic and thermal rates. The radiolytic rate will be determined by subtracting the thermal-only rate from the rate in the presence of external radiation.

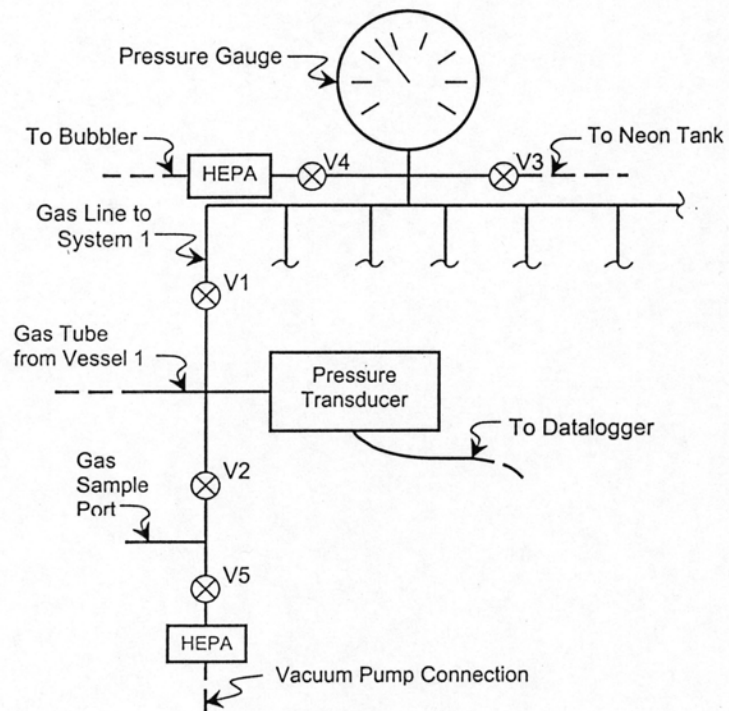
Gas generation measurements will be made using the gas manifold system and procedures developed in the study of Tank 241-SY-103 (Bryan et al 1996) and 241-S-102 (King et al 1997). New reaction vessels will be used for this test and are constructed of 316-L stainless steel. Pressures of each reaction vessel will be measured independently using pressure transducers connected to the gas manifold line of each reaction vessel. The schematic diagram of the gas manifold system with the placement of the reaction vessels relative to the gas manifold system is shown in Figure 1.

Figure 2 illustrates the small-scale reaction vessel and shows where the thermocouples are placed within and outside the vessel. The reaction vessels are 316-L stainless steel cylinders, each internally ~1.75 cm diameter and 14 cm high (internal volume ~33 cm<sup>3</sup>). For the gas generation testing, each vessel will be wrapped in heating tape and insulated. Two thermocouples are attached to the external body, one for temperature control and one for over-temperature protection. Two thermocouples are inserted through the flange. The thermocouple centered in the lower half of the vessel monitored the temperature of the liquid phase; the one centered in the upper half monitored the gas phase temperature within the reaction vessel. The reaction vessels are placed in the hot cell connected by a thin (0.0058-cm inside diameter) stainless steel tube to the gas manifold outside the hot cell. A stainless steel filter (60-micrometer pore size, Nupro) protected the tubing and manifold from contamination. A thermocouple is attached to this filter as well.

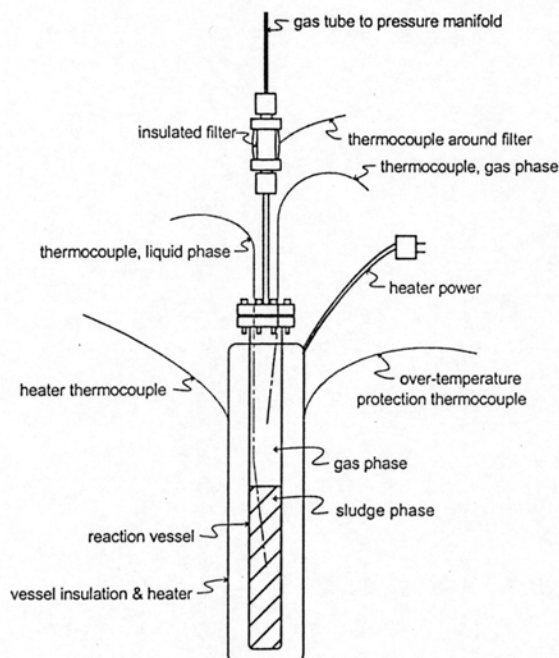
Total moles of gas produced will be calculated based on the measured pressure and temperature and the known volume of the gas phase of the reaction vessel. The volumes of the reaction vessels have been determined gravimetrically using water. The volumes of the pressure sensor, valves, and miscellaneous fittings have been determined from pressure/volume relationships using a calibrated gas manifold system.

Gas samples from the reaction vessels will be withdrawn through the capillary line into an evacuated bulb. The volume of the capillary line is small, less than 2 mL, whereas the gas phase of the reaction vessel volume is ~33 mL in all cases, and the collection bulb volume is ~30 mL. Because gases will move by viscous flow through the capillary tube in this pressure regime, no significant fractionation of the gas is expected.

Analyses to determine the mole percent of the components within the gas phase of each reaction vessel will be performed using the Mass Spectroscopy Facility operated by PNNL in the 325 Building. The amounts of specific gases generated will be calculated from the total moles of gas generated and the mole percent data.



**Figure 1. Pressure Manifold System Used in Gas Generation Tests**



**Figure 2.** Reaction Vessel Used in Small-Scale Gas Generation Tests

### Test Environment

All gas generation testing will be conducted at PNNL's High Level Radiochemistry Facility (325A HLRF) in the RPL facility.

### Data Treatment

Gas generation will be studied both in the presence and absence of an external gamma radiation source ( $^{137}\text{Cs}$  capsule). In both experiments, the rates and composition of gases generated will be measured at three temperatures in duplicate. Separate samples are used for each temperature, and separate samples will be used for the thermal and the radiolytic experiments. Composition of gases generated will be measured by mass spectrometry according to analytical procedure ALO-284, Rev 1.

### Experimental Matrix and Data Analysis

The planned test is expected to generate the data indicated in Table 1. The design variables, temperature ( $^{\circ}\text{C}$ ) and 'Rep' (for replicate) are indicated in the first two columns. The gas generation rate for  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  will be calculated from known volume of the reaction vessel and its contained sample, measured temperature and pressure, and from gas samples taken for analysis for specific gases during the experiment. Gas samples will be taken every three weeks for the  $60^{\circ}\text{C}$  reactions, and more often for the higher temperature reactions.

**Table 1.** Expected Data Matrix from Gas Generation Testing

Temp	Rep	Thermal Gas Gen. Rate (mol/kg/day)						Radiolytic Gas Gen. Rate (mol/kg/day)					
		total	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>	total	H <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>
60°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
75°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
90°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
105°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
120°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—

The analysis of data will provide an empirical fit describing the relationship between the gas generation rate, the temperature applied to the reaction vessel, and the radiation dose. The analysis will account for variability in the temperature for each vessel and the goodness of fit of the statistical model describing the relationship and experimental variability due to any lack of homogeneity in the material sampled and the conduct of the experimental procedure. Since the reactions at each temperature will be duplicated, it will be possible to separate differences due to temperature from the differences due to random variability in the application of the procedure.

#### Quality Control

This work will be performed in accordance with the PNNL's quality assurance plan for its RPP-WTP Project, CHG-QAPjP, Rev. 0, as approved by the RPP-WTP QA organization. The work will be performed in compliance with 10 CFR 830.120, "Quality Assurance Requirements".

The *Quality Assurance Requirements and Description* (DOE/RW-00333P), the principal quality assurance document for the Civilian Radioactive Waste Management Program, does not apply to activities described in this test plan.

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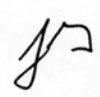
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Wahl, K. L., J. A. Campbell, S. A. Clauss, B. D. Lerner, A. K. Sharma, A. J. Saenz, I. E. Burgeson, R. L. Sell, K. E. Grant, G. M. Mong, C. E. Petersen, S. A. Bryan, and R. D. Scheele. 1995. *Advanced Organic Analysis and Analytical Methods Development: FY 1995 Progress Report*. PNL-10777, Pacific Northwest Laboratory, Richland, Washington.

## **Appendix B**

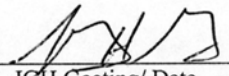
**Battelle Test Instruction TI-RPP-WTP-074 Rev. 1,  
“Energetics and Gas Generation Tests:  
AN-102 Solids Washing”**

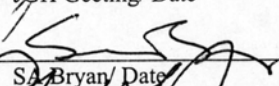
**Test Instruction**      **TI-RPP-WTP-074, Rev. 0/1** 

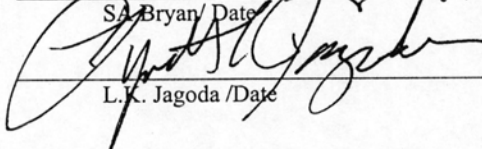
**Effective Date:**      **Upon Approval**

**Controlling Procedure:**      **Test Plan TP-RPP-WTP-066 "Energetics and Gas Generation Tests"**

**TITLE:**      **Energetics and Gas Generation Tests: AN-102 Solids Washing**

Author Approval:  4-23-01  
JGH Geeting/ Date

Author Approval:  4/23/01  
SA Bryan/ Date

Reviewed by:  4/23/01  
L.K. Jagoda /Date

## Applicability

This Test Instruction provides details regarding the implementation of Test Plan TP-RPP-WTP-066 "Energetics and Gas Generation Tests". Specifically it describes how AN-102 solids will be washed prior to Gas Generation and Energetics testing. This document is a mechanism for the cognizant scientist to communicate to technical staff and the client specifics on procedure implementation. Therefore, this document qualifies as a test instruction under Part B Section 16 of the RPL Operations Manual.

Work will be performed by RPL staff under the direction of a cognizant scientist.

Work with actual tank material will be performed in radiological hot cells.

## Justification/Test Objectives/Success Criteria

Solids from sample jars listed in Table 1 will be combined into a composite, washed with 0.01M NaOH, decanted and recombined forming a washed solids composite for use by Test Plan TP-RPP-WTP-066 "Energetics and Gas Generation Tests". The material will be mixed prior to decanting using an agitator for a minimum of one hour. Following decanting the aqueous layer, the solids will then be transferred back into bottles until needed.

Table 1. Solid Samples of AN-102 As-Received Composite

Sample	Mass, g	Volume, ml	Vol% Settled Solids
AN-102 AR-J	585.56	393	67.7
AN-102 AR-K	589.70	396	70.1
AN-102 AR-L	597.11	402	68.4
AN-102 AR-M	604.63	408	68.1
AN-102 AR-N	604.62	405	67.2

No special handling protocols are being used to contain volatile organic compounds.

## Quality Control

This work is to be conducted to the Quality requirements in "Conducting Analytical Work in Support of Regulatory Programs". This quality program can be found on the PNNL internal web site at <http://quality.pnl.gov/Guidance/QualityAssurancePlanning>.

Changes to this test instruction can be made only by a cognizant scientist and will be documented by crossing out the original information on the workplace copy with a single line, and recording, initialing, and dating the changes.

The results of all measurements will be recorded in an LRB, test instruction, or bench sheet. Copies of the completed test instructions, bench sheets, and LRBs will be transferred to the project file upon completion of the test instruction.

### Spill Mitigation

When working with liquids and slurries, there is a risk of sample loss through inadvertent spills. During hot cell work, spills primarily result from dropped or tipped sample bottles, broken glassware, and the failure of transfer equipment. In most cases, spills can be controlled and material losses minimized through the use of secondary containment and other good laboratory practices. The cognizant scientist is responsible for working with hot cell staff to reduce the potential and programmatic impact of spills. Specific examples include:

- 1) Bottle holders to stabilize jars during sample transfers
- 2) Catch pans below homogenization vessels and primary sample containers when reasonably achievable
- 3) Safety coated jars and bottles (when this does not interfere with analytical requirements)
- 4) Plastic centrifuge liners

If a spill does occur, every practical effort will be made to recover as much of the sample as possible.

#### M&TE List:

Balance 1:	Calibration ID <u>L 01015</u>	
	Calibration Expiration <u>2-2002</u>	Location <u>C-Cell</u>
<u>200004 (check with Cal sug. wt)</u>		
Balance 2: (if needed)	Calibration ID _____	
	Calibration Expiration _____	Location _____

Temperature Calibration information if available:

Calibration ID \_\_\_\_\_  
Calibration Expiration \_\_\_\_\_  
Location \_\_\_\_\_

### List of Required Materials

- 2-450 mL bottles pre-labeled AN-102 SOL 1 for storing as-received solids and supernatant (for Solubility task) and AN-102 SOL 2 for storing the supernatant.
- 4-1 liter poly bottles filled with 0.01 M NaOH solution. These bottles shall be labeled AN-102 W-3 thru AN-102 W-6, and will be used to transfer in inhibited water. Later these bottles will be used to store the wash liquor.
- 2-20 mL bottle pre-labeled AN-102 WS 7 and AN-102 WS 8 for storing washed solids (One for Energetics task and one for Paul Bredt)
- One 500 mL "wash bottle" for washing down solids (tare wt. = 313.95 g)
- 450 mL transfer bottle.
- Vacuum decanting system
- 2-50 mL centrifuge bottles. (Tare wt. 11.6 g, each)

### Pre-Start

- Ensure listed materials are available in the hot cell.
- Ensure the tank and agitator are clean.
- Make sure the vacuum decanting system is set up and operational.

### Test Wash

- Add ~25 g of solids to a pre-weighted centrifuge bottle. Weight of empty centrifuge bottle with lid = 11.614 g (a). Weight of bottle with lid and sample = 39.754 g (b). Total sample added (b-a) = 28.140 g (c).

- Make up a counter weight of similar mass and put both in the centrifuge for 15 minutes. Decant liquid into AN-102 SOL 2. Mass of bottle with lid and sample after decanting = 33.897 g (d). Mass of liquid decanted (b-d) = 5.857 g (e). Mass of centrifuged solids (d-a) = 22.283 g (f). Determine the percent mass decrease from centrifugation =  $\frac{(f-e)}{f} \times 100\%$  = 20.81 % (g).

- Add a volume of inhibited water to the centrifuge bottle approximately equal to the solids volume. Record new mass of centrifuge sample with lid. = 50.132 g (h). Mass of inhibited water added (h-d) = 16.235 g (i). 46.932. See note below 4/30/01

- Manually agitate sample until well mixed. Record time wash started 11:25 AM - 4/30/01. Record Cell Temperature 33.8 °C. Agitate sample once every 15 minutes for an hour. with wig-bag vortex mixer

Time agitated  
11:30 AM  
11:45 AM  
12:00

Initials.  
SAB  
SAB  
PER

12:15  
12:30

DER  
DER

After mixing - take wt  
filtered to observe  
mixing - ~3 g  
of sample left  
from tank  
New mass  
of cell sol  
with lid = 46.9  
line(h) above  
Sample was well  
homogenized at the  
point -

- After 1 hour centrifuge sample for 15 minutes. Decant liquid to the 450 mL transfer bottle. Weight of sample after decanting (with lid) = 21.466 g (j). Mass of solids after wash = (j-a) 9.852 g (k).

Tare wt of Transfer Bottle = 314.999 g.



6. Add a volume of inhibited water to the centrifuge bottle approximately equal to the solids volume. Record new mass of centrifuge sample with lid. = 28.251 (l). Mass of inhibited water added (l-j) 6.785 g (m). Total inhibited water added (m+l) = 23.020 (n). Ratio of second to first wash volumes (i/m) = 2.39 (n).
7. Manually agitate sample until well mixed. Record time wash started 2:30 PM. Agitate sample once every 15 minutes for an hour.

Time agitated Initials.  
2:30 PM S.A.B.  
2:45 D.E.R.  
3:00 D.E.R.  
3:15 D.E.R.  
3:30 D.F.K.

8. After 1 hour centrifuge sample for 15 minutes and decant liquid to the 450 mL transfer bottle. Weight of sample after decanting (with lid) = 19.034 (p). Mass of solids after wash = (p-a) 7.420 (q). Percent mass decrease from second washing = initial mass-final mass/initial mass.  $[(f-q)/f] \times 100\%$  24.68 % (r).  
 $\{(9.852 - 7.420)/9.852\} \times 100$
9. By application of the percent mass decrease from centrifugation (g) and percent mass decrease from the washing (r), determine the mass of sample required to end up with 600 g settled solids after washing. Recognize that we will need ~25 g of unwashed solids for Ingrid, 5 g of washed solids for Paul, and 5 g of washed solids for Randy (assuming we are doing both DSC and RSST testing). Then identify which bottles will be used from Table 1.

List those bottles here:

$$\frac{7.42 \text{ g}}{22.25 \text{ g}} \times 100 = 33.297\% - \frac{(600 \text{ g} + 5 \text{ g})}{33.297\%} = 1837 \text{ g total for Sam}$$

Approximate mass and volume of solids to be treated:

Paul Randy  
S.A.B. pre wash  
+ 25 Ingrid  
+ 5  
1857. total unwashed  
solids -  
1857g total

### First Wash

10. Decant the liquid from each of the bottles identified for washing into 450 mL bottle AN-102 SOL 1 (targeted supernatant volume ~200 mL supernatant and 25 g of solids for Ingrid). After decanting, add 25 g of solids to AN-102 SOL 1. Decant remaining supernatant into AN-102 SOL 2. Record weights in the Table 2. Record the wt of decanted samples (AN-102 AR-J thru AN-102 AR-N) in Table 4.

Table 2: Weights of samples containing decanted supernatant.

Jar ID	Weight of empty jar with lid, (g)	Weight of Jar with lid and Supernatant (g)	Weight with Jar, supernatant and solids added, (g)
AN-102 SOL 1	<u>311.10</u> <del>310.23</del>	<u>622.74</u>	<u>647.94</u>
AN-102 SOL 2	314.15		Not applicable

51.101 AN-102 SOL-1 311.10g 375.20g - supernatant from AN-102 AR-J only - decant + sent. prior to adding supernatant from Jars K, L, M, N

64.1g total liquid from J - 5.857g centrifuged

for Ingrid

11. The volume of inhibited water for washing should be approximately equal to the volume of solids to be washed. Record targeted volume of wash solution = 1000 ml(s). Of this volume, add approximately  $\frac{1}{4}$  to the wash tank.

Table 3: Weight of Samples containing Inhibited water—First Wash

Jar ID	Tare weight, (g)	Initial wt (before wash 1)	Final wt (after wash 1)	Inhibited water added for wash 1.
AN-102 W3	104.15	1102.27	(empty) 104.15	998.12 g
<del>AN-102 W4</del>	<del>90.69</del>	<del>1068.61</del>		
AN-102 W5	91.04	1059.08		
AN-102 W6	89.62	1007.83		

Total water added in first wash = \_\_\_\_\_ (t).

12. Add the solids to the tank. Then use the remaining  $\frac{3}{4}$  of inhibited water to wash out jars. Record the mass of solids added to the tank by completing Table 4. Also complete filling out Table 3.

Table 4. AN-102 Core Sample Composite Information

Jar ID	Full Mass of jar and solids with lid (after decant) (g) <i>Before</i>	Empty Mass (g) of jar and lid.	Mass solids Transferred (g)	Mass of decant (g) <i>After</i>
AN-102 AR-J	645.32	311.15	334.17	64.17
AN-102 AR-K	752.28	311.42	331.48	59.38
AN-102 AR-L	733.48	311.50	369.21	52.77
AN-102 AR-M	741.88	311.13	361.83	68.92
AN-102 AR-N	748.73	311.08	370.73	66.92

Record total mass solids transferred = 1817.42 g (u).

13. Turn on agitator to setting 4 and mix for 1 hour. Look into the tank while mixing to verify an adequate mixing pattern. Every 15 minutes put a jar under the drain valve and open to flush out line. Dump contents back into top of tank.

Time Initials  
10:35 S.A.B.  
10:50 - drain - 1 jar & added back - S.A.B.  
11:15 S.A.B. Drain & added back -  
11:30 Drain & added back - S.A.B.  
11:35 mixer off - Allow to settle overnight - S.A.B. -

14. Stop mixer. Place slotted lid with slot cover on the mixing vessel. Let settle



Decant from 1st wash

See attached sheet -  
(73) -

overnight.

Needed  
2 jars -  
decanted  
more than  
2L after  
1st wash

15. Decant using vacuum system. Store decanted first wash liquor in empty 1 liter poly bottles designated AN-102 W 3, 4, 5, or 6 (as appropriate). Record Jar where first wash liquor is stored \_\_\_\_\_. Measure weight of empty container = \_\_\_\_\_. (v). Container plus decanted wash = \_\_\_\_\_. (w). Decanted water (w-v) = \_\_\_\_\_. (x).

### Second Wash

16. Determine the volume of inhibited water for the second wash by multiplying the water used in the first wash (t) by the ratio of second to first wash volumes (n). Targeted volume for second wash (t/n) =  $417.6(y)$ . Before adding any water, fill out the first column of Table 5. Add inhibited water to tank and record final weights in Table 5.

divide rather than multiply  
SAB 5/2/01

$$998.13 / 2.39 = 417.6 g$$

Table 5: Weight of Samples containing Inhibited water—Second Wash

Jar ID	Initial wt, before wash 2, (g) (=Final wt, after wash 1)	Final wt, after wash 2, (g)	Inhibited water added for wash 2.
AN-102 W3	all used for 1st wash		
AN-102 W4	1068.61 <del>1059.08</del>	594.27	474.34
AN-102 W5			
AN-102 W6			

A target mass

actual amt added

AN-102-1st wash  
V2 →

Total water added in second wash = \_\_\_\_\_. (z).

17. Turn on agitator to setting 4 and mix for 1 hour. Look into the tank while mixing to verify an adequate mixing pattern. Every 15 minutes put a jar under the drain valve and open to flush out line. Dump contents back into top of tank.

5/2/01

Time	Initials
11:05am	SAB
11:20	D.B.R
11:37	D.B.R
11:55	D.B.R
12:05	off - mixer - SAB

18. Stop mixer. Place slotted lid with slot cover on the mixing vessel. Let settle overnight.

19. Decant using vacuum system. Store decanted second wash liquor in empty 1 liter poly bottles designated AN-102 W 3, 4, 5, or 6 (as appropriate). Record Jar where first wash

Decant from 1st wash -

	<u>Bottle Label</u>	<u>Tare wt</u>	<u>final wt (with decant)</u>	<u>Decant wt</u>
1st Bottle	AN-102 W3	104.15 g	1205.37 g	1101.2 g
2nd Bottle	AN-102 1st wash $\frac{3}{2}$	$\frac{316}{317.67}$ g	683.98 g	$\frac{366.31}{1446.5}$ g

2nd wash Decant

	<u>Bottle Label</u>	<u>Tare wt</u>	<u>final wt</u>	<u>Decant wt</u>
1st Bottle	AN-102 2nd wash $\frac{1}{2}$	318.44 g	806.78	488.34
2nd Bottle	AN-102 2nd wash $\frac{3}{2}$	218.30	342.86	$\frac{124.56}{612.9}$

3rd wash Decant

	<u>Bottle Label</u>	<u>Tare wt.</u>	<u>final wt</u>	<u>Decant wt</u>
1st Bottle	AN-102-W4	90.69	744.89	654.2

liquor is stored \_\_\_\_\_. Measure weight of empty container = \_\_\_\_\_ (1a).  
Container plus decanted wash = \_\_\_\_\_ (1b). Decanted water (1b-1a) = \_\_\_\_\_ (1c).

### Third Wash

20. The volume of inhibited water for should be approximately equal to the volume of the second wash. Record targeted volume of wash solution = \_\_\_\_\_. Before adding any water, fill out the first column of Table 6. Add inhibited water to tank and record final weights in Table 6.

Table 6: Weight of Samples containing Inhibited water—Third wash

Jar ID	Initial wt, before wash 3, (g) (= Final wt, after wash 2)	Final wt, after wash 3, (g)	Inhibited water added for wash 3.
<del>AN-102 W3</del>	<del>used in 1st wash -</del>		
AN-102 W4	594.27 g	90.69	503.58
AN-102 W5	not used	(not needed)	
AN-102 W6	not used	(not needed)	

Total water added in third wash = \_\_\_\_\_ (1d).

21. Turn on agitator to setting 4 and mix for 1 hour. Look into the tank while mixing to verify an adequate mixing pattern. Every 15 minutes put a jar under the drain valve and open to flush out line. Dump contents back into top of tank.

10:25 start  
Time Initials  
10:45 SWS test drain & added back to tank -  
11:00 DGL  
11:15 DSR  
11:35 DSR

22. Drain washed solids into empty sample bottles AN-102 AR-J thru AN-102 AR-N, as appropriate. Rinse down sides of tank with inhibited water. Mass of inhibited water added = \_\_\_\_\_ (1c). Fill out Table 7.

Table 7: Weights of Washed Solids.

Label	Mass empty (with lid) (g)	Total Mass with lid and sample and supernatant, (g)	Final wt after decanting supernatant, (g)	Final wt of washed solids, (g)
AN-102 AR-J	311.15		560.60	249.45
AN-102 AR-K	311.42		576.55	265.13
AN-102 AR-L	311.50		497.89	186.39
AN-102 AR-M	← Empty			
AN-102 AR-N	Empty			

23. Let samples washed solids from AN-102 AR-J thru AN-102 AR N set over night. Decant any liquid. Third wash decant jar ID = \_\_\_\_\_. Mass of liquid decanted = \_\_\_\_\_. Record final weights of decanted washed solids in Table 7.

24. Get sub-sample for Energetics testing (5 g solids) and for Paul (5 g solids). Make sure the sample is covered with inhibited water. Get final sample in AN-102 WS 9 for PSD. We need ~ 2 mL of slurry. Top the rest of the sample vial off with inhibited water. Record values in the following table.

Target mass	Label	Mass empty (g)	Total Mass with sample (g)	Sample mass (g)
1 g	AN-102 WS 7	16.92	18.57	
5 g	AN-102 WS 8	16.74	23.27	
5 g	AN-102 WS 9	16.75	22.80	

25. Samples AN-102 AR J thru N and AN-102 WS 7 thru 9 will stay in C-cell. Samples AN-102 SOL 1 and 2, and AN-102 W3 thru 6 need to be transferred to SFO, care of Ingrid Burgeson.

SAB 6/13/01  
26.

Sub-sample for chem and Rad-chem analysis. Obtain ~ 5-10 g of "AN-102 AR-K" (washed) from above. Label sample bottle "AN-102 WS-10". Make sure sample is representative of samples used in gas generation testing.

## **Appendix C**

### **Analytical Measurements for AN-102 Samples**

*Battelle PNNL/RSE/Inorganic Analysis ... ICPAES Analysis Report*  
PO Box 999, Richland, Washington 99352

Project / WP#: 42365/ W57955  
ASR#: 6140  
Client: S. Bryan  
Total Samples: 1

RPL#:	01-01474	
Client ID:	AN-102-WS-10- Liquid	
Sample Preparation: Sample prepared by PNL-ALO-128. AOI: Al and Na.		

Procedure: PNNL-ALO-211, "Determination of Elements by  
Inductively Coupled Argon Plasma Atomic Emission  
Spectrometry" (ICPAES).

Analyst: D.R. Sanders

Analysis Date (File): 07-31-01 (A0705)

See Chemical Measurement Center 98620 file: ICP-325-405-1  
(Calibration and Maintenance Records)

M&TE Number: WB73520 (ICPAES instrument)  
360-06-01-029 (Mettler AT400 Balance)

MW Shu 3-14-02  
Reviewed by

Renee Russell  
Concur



*Battelle PNNL/RSE/Inorganic Analysis ... ICPAES Analysis Report*  
PO Box 999, Richland, Washington 99352

One liquid sample (RPL# 01-01474) submitted under Analytical Service Request (ASR) 6140 was prepared by acid digestion per PNL-ALO-128. The sample was digested in the Shielded Analytical Laboratory by using 1.0 mL of sample and diluting to a final volume of 25 mL. Analytes of interest (AOI) were specified on the ASR as Al and Na. All other analytes that were not requested are reported, but have not been fully evaluated for QC performance.

A summary of the ICPAES analyses of the sample, including QC performance, is given in the attached ICPAES Data Report (2 pages). ICPAES measurement results are reported in  $\mu\text{g/mL}$  and have been corrected for dilution resulting from sample processing.

The process blank had detectable amounts of both Al and Na present. The Al was below estimated quantitation limits (EQL). The Na present in the process blank was at a concentration less than 5% of the sample concentration. The Na concentration in the process blank is approximately 0.2% of that found in the AN-102-WS-10-Liquid sample.

Quality control check-standard results met tolerance requirements for the specific AOI's except as noted below. Following is a list of quality control measurement results relative to ICPAES analysis tolerance requirements of the controlling QA plan. Blank spikes, matrix spikes and duplicates were prepared with the sample and analyzed. Blank spike and matrix spike samples were prepared using 3 mL for the blank spikes and 1 mL for the matrix spikes of multi-element solution "TW Spike Part 2" per 25 mL of digestate volume.

Process Blanks:

The concentration of the analytes of interest measured in the process blank were within the tolerance limit of  $\leq \text{EQL}$  or less than  $\leq 5\%$  of the sample concentration.

Duplicate RPD (Relative Percent Difference):

The original and duplicate sample (RPL# 01-01474) were within tolerance limit of  $\leq 20\%$  RPD for all analytes of interest.

Blank Spike:

Blank spike recovery for Al was within tolerance of 80% to 120%. The blank spike recovery for Na was outside the tolerance limit at 127%. However, a single element Na 1000 ppm standard recovered at 100% and 99% during the analysis run.

Matrix Spiked Sample:

Matrix spike recovery for Al was within the tolerance limit of 75% to 125%. Sodium recovery was not calculated since the Na spike concentration was less than 20% of the sample concentration.

Post-Spiked Samples (Group A):

The sodium recovery in the post spiked sample (Group A) was 130%. This is outside the tolerance limit if 75% to 125%. All other analytes were within the tolerance limit.

Post-Spiked Samples (Group B):

All analytes recovered in the post spiked sample (Group B) were within the tolerance limit of 75% to 125%. There were no analytes of interest in this sample.

Five fold serial dilution:

All analytes above the EQL, including Na, in the sample tested were within tolerance limit of 10% after correcting for dilution.

Other Quality Control Standards:

Both the Al and Na were outside the tolerance limits in the calibration blank standard.

Analytes other than those requested by the client are for information only. Please note bracketed values listed in the data report are within ten times instrument detection limit and have a potential uncertainty much greater than 15%.

Comments:

- 1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.
- 2) Detection limits (DL) shown are for acidified water. Detection limits for other matrices may be determined if requested.
- 3) Routine precision and bias is typically  $\pm 15\%$  or better for samples in dilute, acidified water (e.g. 2% v/v HNO<sub>3</sub> or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000  $\mu\text{g/mL}$  (0.5 per cent by weight).
- 4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
- 5) The maximum number of significant figures for all ICP measurements is 2.



	Run Date=	7/31/2001	7/31/2001	7/31/2001	7/31/2001
	Multiplier=	25.2	25.0	124.8	126.2
	RPL/LAB #=	01-1474-B	01-1474	01-1474 @5	01-1474-DUP @5
Det. Limit	Client ID=	Process Blank	AN-102-WS-10-Liquid	AN-102-WS-10-Liquid @5	AN-102-WS-10-Liquid-Dup
(ug/mL)	(Analyte)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)
0.060	Al	[7.8]	1,270		1,290
0.150	Na	106	na	52,600	52,500
Other Analytes					
0.025	Ag	--	--		--
0.250	As	--	--		--
0.050	B	69.3	98.4		80.4
0.010	Ba	--	--		--
0.010	Be	--	--		--
0.100	Bi	--	--		--
0.250	Ca	--	104		[110]
0.015	Cd	--	11.5		[12]
0.200	Ce	--	--		--
0.050	Co	--	--		--
0.020	Cr	--	75.8		78.7
0.025	Cu	--	[4.4]		[3.8]
0.050	Dy	--	--		--
0.100	Eu	--	--		--
0.025	Fe	[1.5]	[3.3]		[3.3]
2.000	K	--	[410]		[330]
0.050	La	--	--		--
0.030	Li	--	--		--
0.100	Mg	--	--		--
0.050	Mn	--	--		--
0.050	Mo	--	[11]		[11]
0.100	Nd	--	[3.4]		--
0.030	Ni	[6.7]	87.3		90.8
0.100	P	--	384		381
0.100	Pb	--	46.6		[46]
0.750	Pd	--	--		--
0.300	Rh	--	--		--
1.100	Ru	--	--		--
0.500	Sb	--	--		--
0.250	Se	--	--		--
0.500	Si	[120]	153		[130]
1.500	Sn	--	--		--
0.015	Sr	--	--		--
1.500	Te	--	--		--
1.000	Th	--	--		--
0.025	Ti	--	--		--
0.500	Tl	--	--		--
2.000	U	--	--		--
0.050	V	--	--		--
2.000	W	--	--		--
0.050	Y	--	--		--
0.050	Zn	--	--		--
0.050	Zr	--	--		--

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

## QC Performance 7/31/2001

Criteria>	<20% <sup>(a)</sup>	80% - 120%	75%-125%	75%-125%	75%-125%	< +/-10%	< +/-10%
QC ID=	01-01474 @5 & 01-01474-D @5	LCS/BS	01-01474 & 01-01474-MS	01-01474 + Post Spike A	01-01474 + Post Spike B	01-01474 @1/@5 Serial Dil	01-01474 @5/@10 Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff	%Diff
Al	-0.4	117	120	103		1.5	
Na	-0.8	127	nr	130		na	4.2
Other Analytes							
Ag				100			
As				106			
B	-22.9			104		2.1	
Ba		125	125	103			
Be				102			
Bi		117	118	103			
Ca		116	123	102		3.1	
Cd		115	116	104		3.2	
Ce					102		
Co				108			
Cr	0.4	120	143	106		2.7	
Cu		119	118	107			
Dy					103		
Eu					111		
Fe		125	nr	107			
K		112	110	99			
La		117	119		100		
Li				101			
Mg		121	126	111			
Mn		119	127	107			
Mo				105			
Nd					101		
Ni	-3.6	118	137	107		6.6	
P	-1.2	114	116	102		-0.3	
Pb		121	124	108		1.0	
Pd		117	111		89		
Rh		118	115		97		
Ru		113					
Sb				104			
Se				106			
Si		153	133	115		21.3	
Sn							
Sr		118	119	104			
Te							
Th					102		
Ti		114	113	100			
Tl				103			
U		119	115		100		
V				102			
W							
Y				103			
Zn		118	124	108			
Zr		118	118	104			

Shaded results exceed acceptance criteria

(a) Na RPD Criteria  $\leq 3.5\%$ 

Bold results for information only; LCS, MS, PS, or Serial Dilution concentration less than EQL

n.r. = not recovered; spike concentration less than 20% of sample concentration

n/a = not applicable; Value greater than upper calibration limit

**Battelle PNNL/RSE/Inorganic Analysis ... ICPAES Analysis Report**  
**PO Box 999, Richland, Washington 99352**

Project / WP#: 42365 / W57955  
ASR#: 6140  
Client: S. Bryan  
Total Samples: 1 (solids sample only)

RPL#:	01-01475	
Client ID:	"AN-102-WS-10-Solids"	
Sample Preparation: PNL-ALO-129 (0.5g/25mL)		

Procedure: PNNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry" (ICPAES).

Analyst: D.R. Sanders

Analysis Date (File): 07-18-2001 (A0700)

See Chemical Measurement Center 98620 file: ICP-325-405-1  
(Calibration and Maintenance Records)

M&TE Number: WB73520 (ICPAES instrument)  
360-06-01-029 (Mettler AT400 Balance)

MW Zhu 9-14-01

Reviewed by

Jerry Wagner 9-18-01

Concur

## **Battelle PNNL/RSE/Inorganic Analysis ... ICPAES Analysis Report**

Sample AN-102-WS-10 was phase separated by centrifuging in the Shielded Analytical Laboratory (SAL). This report includes the results from the solids phase, sample 01-1475 (AN-102-WS-10-Solids); the results of the liquid phase, sample 01-1475 (AN-102-WS-10-Liquid), are reported under separate cover. The AN-102-WS-10-Solids sample was digested in the SAL using PNL-ALO-129 acid digestion for solids. Approximately 0.5 g of the AN-102-WS-Solids was digested and diluted to a final volume of approximately 25 mL (with the actual volume being determined by mass and density of the digestate).

Per discussion with the Analytical Service Request (ASR) requestor, only Al and Na were identified as analytes of interest for this work. However, the ASR included Table 2 'Solid Fraction Analysis' from TSP-W375-01-00002 which identifies Ag, Al, Ba, Bi, Ca, Cd, Cr, Du, Fe, La, Mg, Mn, Na, Nd, Ni, P, Pb and Si as being the analytes of interest for solids; therefore, the ICPAES analyte of interest list has been expanded to include these analytes. The quality control (QC) results for each of these analytes has been evaluated and is presented below. Analytes other than those identified in Table 2 in the ASR were measured as part of the ICPAES analysis; however, these analytes are reported for information only, since the QC performance has not been fully evaluated.

The attached ICPAES Results (2 pages) presents the final results. All results are from measurement of the digestates following an additional 10x dilution at the ICPAES, which was required to bring the high concentration analytes into the linear calibration range. The ICPAES measurement results are reported in  $\mu\text{g/g}$  of wet centrifuged solids and have been corrected for all dilutions resulting from sample processing.

The following is a list of quality control measurement results relative to ICPAES analysis tolerance requirements of the controlling QA plan. A digestion processing blank, laboratory control sample (blank spike), duplicate, and matrix spike were prepared with the sample. The blank spike was prepared by using nominally 5 mL of a custom multi-element solution "INT-QC-MCVA-1B" per 25 mL sample digestate volume and the matrix spike was prepared using the same multi-element solution but at 2 mL per 25 mL of digestate.

### Process Blank:

Concentration of analytes of interest measured in the process blank were all within tolerance limit of  $\leq \text{EQL}$  or less than  $\leq 5\%$  of the concentration in the sample.

### Blank Spike (laboratory control sample):

The blank spike recovery for analytes of interest was within the acceptance criteria of 80% to 120%.

### Duplicate RPD (Relative Percent Difference):

For those analytes of interest measured above the estimated Method Detection Limit (MDL), the RPDs were within the acceptance criteria of less than 20%. Silicon, which is not digested well by the PNL-ALO-129 acid digestion procedure, showed the largest sample to duplicate variation with an RPD of about 10%.



## **Battelle PNNL/RSE/Inorganic Analysis ... ICPAES Analysis Report**

### Matrix Spiked Sample:

The matrix spike recoveries for the analytes of interest fall into four categories. 1) those analytes for which a matrix spike element was not included in the matrix spiking solution (i.e., La, Nd and Si, 2) those analytes that have spike concentrations less than 20% of the sample concentration (i.e., Al, Ba, Cr, Fe, Mn, Na, P, and Pb) making the spike recovery calculation meaningless, 3) those analytes that failed to meet the acceptance criteria of 75% to 125% (i.e., Ni), and 4) those analytes that demonstrated matrix spike recoveries within the acceptance criteria (i.e., all other analytes of interest). For those analytes falling into categories 1), 2), and 3), post spiking of the digestate (or in some cases serial dilution) is used to evaluate matrix interference issues.

### Post-Spiked Samples (Group A: all analytes of interest except La)):

All post-spiked analytes of interest in samples tested were recovered within tolerance of 75% to 125%, except Al, Cr, Mn, and Na. The post spike analysis uses a general spiking solution intended to be usable on the majority of sample analyzed by ICPAES. However, for the sample selected for post spiking, the spike concentration for Al, Cr, Mn, and Na was less than 20% of the sample concentration and the recovery results are considered meaningless. For these analytes, the use of serial dilution results is required to evaluate potential matrix interferences.

### Post-Spiked Samples (Group B: La and Nd only):

The post spiked La and Nd was recovered within tolerance of 75% to 125%.

### Serial dilution:

Serial dilution was required for Al, Cr, Mn, and Na, since both the matrix spike and post spike concentrations were less than 20% of the sample concentration (i.e., recoveries could not be evaluated). These analytes demonstrated a percent difference (%D) within the acceptance criteria of  $\pm 10\%$  after correcting for dilution. However, sodium was right at the upper limit,

### Comments:

- 1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.
- 2) Detection limits (Det. Limit) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the 'Multiplier' times the Detection Limit.
- 3) Routine precision and bias is typically  $\pm 15\%$  or better for samples in dilute, acidified water (e.g. 2% v/v HNO<sub>3</sub> or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000  $\mu\text{g/mL}$  (0.5 per cent by weight). Note that bracketed values listed in the data report are within ten times instrument detection limit (adjusted for processing factors and laboratory dilutions) and have a potential uncertainty much greater than 15%.
- 4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
- 5) The maximum number of significant figures for all ICP measurements is 2.

Det. Limit	Multiplier=	51.1	517.5	549.1
	RPL#=	01-1475-B	01-1475	01-1475 D
	Client ID=	Process Blank	AN-102-WS-10-Solids	AN-102-WS-10-Solids
	ug/mL	ug/mL	ug/g	ug/g
0.025	Ag	--	--	--
0.060	Al	[13]	166,000	165,000
0.010	Ba	--	215	215
0.100	Bi	--	--	--
0.250	Ca	--	[470]	[460]
0.015	Cd	--	[35]	[35]
0.020	Cr	[5.7]	12,200	12,100
0.025	Cu	--	[34]	[33]
0.025	Fe	24.3	8,340	8,310
0.050	La	--	[180]	[180]
0.100	Mg	--	[82]	[85]
0.050	Mn	--	1,850	1,840
0.150	Na	171	192,000	195,000
0.100	Nd	--	[380]	[380]
0.030	Ni	[4.8]	173	174
0.100	P	--	2,700	2,510
0.100	Pb	--	914	895
0.500	Si	324	[760]	[690]
Other Analytes Detected				
0.050	B	104	[220]	[210]
0.200	Ce	--	[140]	[130]
0.015	Sr	--	[39]	[39]
0.050	Y	--	[57]	[57]
0.050	Zn	--	[130]	[130]
0.050	Zr	--	315	[56]
Other Analytes Measured but Not Detected				
0.250	As	--	--	--
0.010	Be	--	--	--
0.050	Co	--	--	--
0.050	Dy	--	--	--
0.100	Eu	--	--	--
2.000	K	--	--	--
0.030	Li	--	--	--
0.050	Mo	--	--	--
0.750	Pd	--	--	--
0.300	Rh	--	--	--
1.100	Ru	--	--	--
0.500	Sb	--	--	--
0.250	Se	--	--	--
1.500	Sn	--	--	--
1.500	Te	--	--	--
1.000	Th	--	--	--
0.025	Ti	--	--	--
0.500	Tl	--	--	--
2.000	U	--	--	--
0.050	V	--	--	--
2.000	W	--	--	--

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

*Solids*

QC Performance

Criteria>	<20%	80% - 120%	75%-125%	75%-125%	75%-125%	< +/-10%
QC ID=	01-1475 & 01-1475 D	01-1475-BS	01-1475 MS	01-1475 + Post Spike A	01-1475 + Post Spike B	01-1475 @5/@25 Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Ag		94.4	116.4	97.2		
Al	0.5	97.7	n.r.	n.r.		-1.5
Ba	0.2	97.9	n.r.	104.0		
Bi		94.1	98.3	97.8		
Ca	1.0	95.3	94.8	101.1		
Cd	0.8	96.0	81.5	99.7		
Cr	0.9	92.9	n.r.	n.r.		-4.1
Cu	3.3	99.9	87.7	102.2		
Fe	0.4	98.3	n.r.	104.5		-3.6
La	1.2				99.4	
Mg	3.5	99.1	102.2	105.5		
Mn	0.7	100.5	n.r.	n.r.		-3.3
Na	1.3	104.8	n.r.	n.r.		-9.8
Nd	1.3				101.6	
Ni	0.2	97.9	57.2	103.0		
P	7.5	95.0	n.r.	94.4		
Pb	2.1	98.6	n.r.	101.9		
Si	10.2			109.7		
Other Analytes						
B	7.3	101.6	68.3	103.2		
Ce	3.0				100.4	
Sr	0.2	98.9	83.9	105.0		
Y	0.8	92.0	78.0	97.7		
Zn	0.0	100.2	70.0	104.7		
Zr	140.0			110.7		
Other Analytes Measured but Not Detected						
As		95.4		87.7		
Be		95.4	194.6	99.2		
Co		98.6	96.3	102.4		
Dy					102.1	
Eu					109.3	
K		102.7	121.9	106.3		
Li		106.0	112.6	109.6		
Mo				103.9		
Pd					97.8	
Rh					100.6	
Ru						
Sb				89.6		
Se		97.3		98.2		
Sn						
Te						
Th					102.9	
Ti				99.3		
Tl		92.6		87.9		
U					95.8	
V		92.1	95.8	96.0		
W						

n.r. = not recovered; spike at <20% of sample concentration

## Battelle PNNL/RPG/Inorganic Analysis --- IC Report

Client: S. Bryan  
ASR Number: 6140  
Sample Prep Date: N/A  
Analyst: MJ Steele

Charge Code/Project: W57955 / 42365  
Sample Receipt Date: 06/20/2001  
Sample Analysis Date: 09/24/2001

Preparation Procedure: For solids, PNL-ALO-103, "Water Leach of Sludges, Soils, and Other Solid Samples"  
Procedure: PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography"  
M&TE: IC system (WD25214); Balance (360-06-01-031) --- See Chemical Measurement Center  
98620 RIDS IC File for Calibration, Standards Preparations, and Maintenance Records.

RPL	Liquid Sample ID	F <sup>(1)</sup> ug/ml	Cl Ug/ml	NO <sub>2</sub> ug/ml	Br ug/ml	NO <sub>3</sub> ug/ml	PO <sub>4</sub> ug/ml	SO <sub>4</sub> ug/ml	C <sub>2</sub> O <sub>4</sub> ug/ml
	<i>EQL</i>	<i>0.14</i>	<i>0.14</i>	<i>0.28</i>	<i>0.14</i>	<i>0.28</i>	<i>0.28</i>	<i>0.28</i>	<i>0.28</i>
01-01475	Hot Cell Processing Blank	< 0.14	< 0.14	< 0.28	< 0.14	< 0.28	< 0.28	< 0.28	< 0.28
	<i>EQL</i>	<i>63</i>	<i>63</i>	<i>630</i>	<i>310</i>	<i>630</i>	<i>130</i>	<i>130</i>	<i>130</i>
01-01474	AN-102-WS-10-Liquid	1,690	850	19,500	< 310	46,800	1,290	4,880	4,960
01-01474 Dup	AN-102-WS-10-Liquid Dup	1,650	820	18,600	< 310	44,300	1,220	4,800	4,620
	RPD	2	4	5	n.a.	5	6	2	7
	Blank Spike (LCS) %Rec	102	101	100	104	96	102	99	106
01-01474 MS	AN-102-WS-10-Liquid MS % Rec	102	96	99	98	94	95	95	100
RPL	Solid Sample ID	F <sup>(1)</sup> ug/g	Cl ug/g	NO <sub>2</sub> ug/g	Br ug/g	NO <sub>3</sub> ug/g	PO <sub>4</sub> ug/g	SO <sub>4</sub> ug/g	C <sub>2</sub> O <sub>4</sub> <sup>(2)</sup> ug/g
	<i>EQL</i>	<i>11</i>	<i>11</i>	<i>22</i>	<i>11</i>	<i>22</i>	<i>22</i>	<i>22</i>	<i>22</i>
01-01475	Hot Cell Processing Blank	< 11	< 11	< 22	< 11	< 22	< 22	< 22	< 22
	<i>EQL</i>	<i>64</i>	<i>64</i>	<i>1,300</i>	<i>640</i>	<i>1,300</i>	<i>130</i>	<i>130</i>	<i>130</i>
01-01475	AN-102-WS-10-Solids	1,670	750	17,500	< 640	38,800	3,220	4,260	104,000
	<i>EQL</i>	<i>45</i>	<i>45</i>	<i>900</i>	<i>450</i>	<i>900</i>	<i>45</i>	<i>900</i>	<i>900</i>
01-01475 Dup	AN-102-WS-10-Solids Dup	1,870	730	19,100	< 450	43,700	3,280	6,000	119,000
	RPD	11	3	9	n.a.	12	2	34	13
	HC Blank Spike (LCS) %Rec	126	132	132	132	129	130	134	0
01-01475 MS	AN-102-WS-10-SolidsMS % Rec	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
01-01475 PS	AN-102-WS-10-Solids PS % Rec	97	103	90	102	70	100	98	25

n.r. = not recovered; matrix spike concentration less than 20% of sample concentration.

n.a. = not applicable; sample and/or duplicate concentration less than the EQL; RPD not calculated.

- (1) The fluoride results should be considered the upper bound concentration for the fluoride. Significant peak distortion of the fluoride peak suggests the presence of co-eluting anion(s), possibly formate or acetate.
- (2) The oxalate peak demonstrates significant peak tailing; high uncertainty in reported concentration.

The liquid sample was prepared for ion chromatography anion analysis by diluting to ensure that the anions were measured within the calibration range and that the IC column was not overloaded during the analysis. Sample 01-01474 required dilutions from 500-fold (F, Cl, PO<sub>4</sub>, and SO<sub>4</sub>) to 2,500-fold (all other anions). Solid Sample 01-01475 was leached in the Shielded Analytical Laboratory hot cells at approximately 75 to 1 with distilled, deionized water. Following this leaching the sample required additional dilution to ensure that the anions were measured within the calibration range. This sample required dilutions from 5.5-fold (F, Cl, PO<sub>4</sub>, SO<sub>4</sub>, and C<sub>2</sub>O<sub>4</sub>) to 55-fold (NO<sub>3</sub> and NO<sub>2</sub>). The estimated quantitation limit (EQL) which are based on the lowest calibration standard and the dilutions used for reporting the results are provided in the table.

### Q.C. Comments:

Duplicates: Both the liquid and solids samples were prepared and analyzed in duplicate. The duplicate relative percent difference (RPD) meets the acceptance criteria of <20% of the QA plan sections defined by



## **Battelle PNNL/RPG/Inorganic Analysis --- IC Report**

the ASR, except for the solids phosphate duplicate results (i.e., RPD = 34%). The poor reproducibility of the phosphate is likely due to solids sample heterogeneity and poor solubility of phosphates.

### **LIQUID**

Laboratory Control Sample/Blank Spike (CCV 010912 @2x): A Blank Spike was prepared from the mid-range continuing calibration verification standard and demonstrated recoveries within the 80% to 120% acceptance criteria.

Liquid Matrix Spike (HCV 010912 @2x): A matrix spike was prepared from AN-102-WS-10-Liquid and all anion recoveries were within the 75% to 125% recovery acceptance criteria.

### **SOLIDS**

Laboratory Control Sample/Blank Spike (MS-010517 @15x): A Blank Spike was prepared in the hot cells from the leach matrix spike standard. The blank spike was processed identically to the samples (i.e., leached/stirred) and demonstrated recoveries exceeding the 80% to 120% acceptance criteria. In all cases, except oxalate, this hot cell blank spike had recoveries from 126% to 134%, perhaps through a rapid evaporation during the preparation activities. The loss of the oxalate was unexpected and can not be explained; however, this loss is under further investigation. The very high oxalate values for the solids samples suggests that the oxalate loss may be restricted to the blank spike (see Post Spike discussion).

Solids Matrix Spike (MS-010517 @15x): A matrix spike was prepared from AN-102-WS-10-Solids assuming that no additional dilution would be required following the 57 to 1 leaching of the solids. The solids matrix spike was unusable due to 1) the spiking levels were <20% of the sample concentration or 2) the additional dilutions required for the sample analysis diluted the matrix spike to below the EQL.

Solids Post Spike (HCV 010912 @2x): Following the failure to recover the matrix spikes, a post spike was prepared from the AN-102-WS-10-Solids leachate. Except for nitrate and oxalate, the anions recoveries were within the acceptance criteria of 75% to 125%. The nitrate post spike recovery of 70% is close to the lower acceptance limit. The oxalate post spike recovery is impacted by the very high sample to spike concentration ratio; however, no additional post spike were prepared using more highly diluted leachate.

### **General Comments:**

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- The low calibration standards are defined as the estimated quantitation limit (EQL) for the reported results and assume non-complex aqueous matrices. Actual detection limits or quantitation limits for specific sample matrices may be determined, if requested.
- Routine precision and bias are typically  $\pm 15\%$  or better for non-complex aqueous samples that are free of interference and have similar concentrations as the measured anions.

Report Prepared by:

*MW Chy*

Date 1-3-02

Review/Approval:

*Marilyn J Steele*

Date 1-8-02

**Excel Archive Information:** ASR 6140.xls

**Screening Archive Information:** Filed with ASR 6164 IC data (Project 42365)

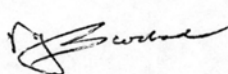


Date: 09/21/01

Subject: Hydroxide Analyses for: AN-102 Phase Separations  
ASR: 6140

To: Sam Bryan

From: Bob Swoboda

 9/21/01

Liquid and water leached solid samples of **AN-102 tank waste** were analyzed in duplicate for the hydroxide content following procedure PNL-ALO-228. Direct sample aliquots for the liquid fraction (01-1474) and two leached solid samples (01-1475 and 01-1475-dup) were analyzed using a Brinkman 636 Auto-Titrator. A 0.1186 N NaOH (ChemRec\_55) solution was used as a standard and sample spike and the titrant was a 0.2040 M HCl prepared solution for the liquid fraction. A 0.0103 N NaOH (ChemRec\_72), solution was used as a standard and sample spike and the titrant was a 0.0051 M HCl prepared solution for the solid leachates. The attached Report Summary indicates good RPD on the OH molarity (1st inflection point) on the sample and replicate results. The hydroxide results were all well below the required MRQ value of 7.5E+04 ug/mL for the liquid phase and MRQ value of 7.5E+04 ug/g for the solid leachates. The molarities at all 3 inflection points on the water leached solid sample and sample duplicate were adjusted by the hot cell dilution factor to convert the results to ug/g of solid starting material. The hydroxide recoveries averaged 100% for the standards and the matrix spike recovery on 01-1474 was 102% and the matrix spike recovery on 01-14754 was 94%. No hydroxide was detected in the reagent blank. The second and third inflection points frequently associated with carbonate and bicarbonate, showed excellent RPD for the liquid phase and also good RPD for the solid leach considering the weak acid concentration required here. All of the results meet the QC acceptance criteria for spike recovery and RSD of duplicate measurements. The titration curves are included with the report.

Review: LR Greenwood 9-21-01

Battelle Pacific Northwest Laboratory  
Radiochemical Processing Group-325 Building  
Chemical Measurements Center

ASR # **6140**

WP# **W57955**

Hydroxide and Alkalinity Determination

Procedure: PNL-ALO-228

Equip #

**WB76843**

**Report Summary for ASR # --**

**6140**

RPG #	Client ID		OH conc ug/mL	Concentration, moles				RPD	RPD	RPD
				First Point		Second Point				
		Liquids								
01-1474	AN-102-WS-10 -Liquid		1.3E+03	0.08		0.49			0.44	
01-1474	AN-102-WS-10 -Liquid	Rep	1.5E+03	0.09	10%	0.48	3%		0.45	1%
		Solids								
			ug/g							
01-1475	AN-102-WS-10 -Solid		5.6E+03	0.33		0.31			0.79	
01-1475	AN-102-WS-10 -Solid	Rep	5.6E+03	0.33	0%	0.35	11%		0.64	22%
01-1475-dup	AN-102-WS-10 -Solid		7.6E+03	0.45		0.34			0.63	
01-1475-dup	AN-102-WS-10 -Solid	Rep	7.6E+03	0.45	0%	0.35	5%		0.64	1%

Reag. Blk.1	0
Standard 1	99%
Standard 2	101%
Standard 3	99%
Standard 4	100%
MS 01-1474 Matrix spike	98%
MS 01-1475 Matrix spike	94%

Note: Results are presented for the first, second, and third inflection points on the titration curves, as applicable. The first inflection point is generally associated with the hydroxide concentration. The second and third points generally represent the carbonate and bicarbonate concentrations.

Analyst: *Ng B...* 9-21-01

Reviewer: *L. H. ...* 9-21-01

Battelle Pacific Northwest Laboratory  
Radiochemical Processing Group-325 Building

ASR # **6140**  
Client: Sam Bryan  
WP# **W57955**

File: R:\radchem\hydroxide\asr 6140  
Analysis Date: **09/19/01**  
Report Date: **09/21/01**

Procedures: **RPG-CMC-228: Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates and Operation of Brinkman 636 Auto-Titrator**  
Equip # **WB76843** Lab Loc. **525**

Analyst: *J. S. ... 9/21/01*

RPG #	Sample ID	Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Sample Density g/mL	Titrator Routine #	Initial pH reading	OH		Found millimoles base	Molarity base	millimole RPD
								1st Equivalence Point	Titrant			
								Vol. (mL)	pH			
01-1475-Blk	AN-102-WS-10 -Blk	na	1.000	1.0000	1.000	29	5.150	none				
01-1474	AN-102-WS-10 -Liquid	na	0.500	0.5646	1.129	26	11.685	0.191	11.107	0.039	0.08	
01-1474	AN-102-WS-10 -Liquid	Replicate	na	0.500	0.5564	27	11.678	0.211	11.026	0.043	0.09	9.95%
Changed to a weaker acid to complete this analysis (0.0051M HCl)												
01-1475	AN-102-WS-10 -Solid	92.69	0.500	0.5018	1.004	36	10.130	0.349	8.891	0.165	0.33	
01-1475	AN-102-WS-10 -Solid	Replicate	92.69	1.000	1.0010	1.001	37	10.186	0.701	8.916	0.331	0.43%
01-1475-dup	AN-102-WS-10 -Solid	65.38	1.000	1.0012	1.001	38	10.430	1.341	8.892	0.447	0.45	
01-1475-dup	AN-102-WS-10 -Solid	Replicate	65.38	0.500	0.5053	1.011	10.271	0.671	8.833	0.224	0.45	0.07%
											0.0068	
Reag. Blk.1			5.00			1	5.058			OH % Recovery		
Standard 1	0.1186 N NaOH		2.500	2.533	1.013	2	12.354	1.438	10.359	0.2934	98.9%	
Standard 2	0.1186 N NaOH		2.500	2.5204	1.008	3	12.398	1.475	7.649	0.3009	101.5%	
Standard 3	0.0103 M NaOH		2.000	2.0033	1.002	34	11.700	4.009	8.203	0.0204	99.3%	
Standard 4	0.0103 M NaOH		2.000	2.0026	1.001	35	11.613	4.026	8.124	0.0205	99.7%	
MS 01-1474	01-1474+ 2mL 0.1N NaOH		0.300	0.3361	1.120	28	12.485	1.26	11.065	0.2570	98.0%	MS
MS 01-1475	01-1475 + 1mL 0.01N NaOH		0.200	0.2008	1.004	40	10.997	2.173	8.446	0.0111	94.3%	MS

Buffer	JT Baker Lot #	CMS#	Expire Date
10	J38505	161304	Sep-02
4	V0510	161306	Jan-03
7	J34512	161305	Aug-02
Initial	pH 7.0 reading =	7.003	
Continuing	pH 7.0 reading =	7.021	

Performance checks using Balance # 360--01-06-037					
Pipet #	Vol.	Wt.	Pipet #	Vol.	Wt.
F04171	2.50	2.5012	122118	0.500	0.4992
F04171	2.50	2.4958	122118	0.500	0.4988
F04171	2.50	2.5041	122118	0.500	0.4973
273494	0.200	0.1984	223382	0.100	0.0994
273494	0.200	0.1968	223382	0.100	0.0986
273494	0.200	0.1995	223382	0.100	0.0998





## Chem Rec\_72

Prep date: 6/21/01

## Preparation and Standardization 0.02 and 0.005 M HCl

WP# K88426

for: RPL-CMC- OH analysis

Prepare 1- liter supply of 1M HCL and 0.2M HCl  
 Calculation:  $1000 \text{ mL} \times 1.0 \text{ N HCl} / 12 \text{ M HCl} = 83.33 \text{ mL of } 12 \text{ N HCl diluted to 1 liter with H}_2\text{O}$ .  
 0.2 M HCl is a 1 : 5 dilution of 1M HCl  
 Used 83.5 mL reagent grade conc HCl (Barcode # 58914) and diluted to 1000 mL using nanopure (Type II ASTM grade) water. The 0.02M HCl was prepared by diluting 20 mL of 1M HCl to 1Liter  
 The 0.005 M HCl was prepared by diluting 5 mL of 1M HCl to 1Liter  
 The 0.02 M HCl will be titrated against standardized 0.1005M NaOH solution (Chem Rec\_64), then used to standardized ~0.01M NaOH and then used to set  
 50 mL aliquots of 0.2 M HCl were were neutralized to the phenolphthalein endpoint using the recently standardized 0.1005 M NaOH. The volume of NaOH is accurate to +/- 0.02mL and the pipetting error is estimated to be <0.3% @ 1s. Thus total error @ 1sigma is combined pipetting and titration error (i.e. Molarity error plus pipeting error ~0.3%)

## NaOH Molarity verification --- from Chem Rec -64

Verification Test #	(target = .41g) Wt. of KAP	Vol. Of ~ 0.1M NaOH to neutralize	NaOH Molarity = $a \times 1000 / b \times 204.23$	Molarity Error +/- @ 1 s
1	0.40071	19.5	0.10062	
2	0.43252	21.1	0.10037	
3	0.41742	20.35	0.10044	
Ave=			0.10047	0.00013
			certified value	0.13%

## Hydrochloric Acid Molarity

Titration Id.	aliquot of acid	Vol. of 0.1005M NaOH to neutralize	Molarity of Acid in Sample	Molarity Error +/- @ 1 s
1	50.00	10.10	0.0203	
2	50.00	10.04	0.0202	
3	50.00	10.15	0.0204	
Ave Molarity =			0.0203	0.00011

0.55%

Expires 6-21-2002

## using Hydrochloric Acid set Molarity of more dilute NaOH

Titration Id.	aliquot of acid	Vol. of 0.01M NaOH to neutralize	Molarity of NaOH in Sample	Molarity Error +/- @ 1 s
1	10.00	19.50	0.0104	
2	10.00	19.80	0.0102	
3	20.00	39.20	0.0103	
Ave Molarity =			0.0103	0.00008

0.78%

## Hydrochloric Acid Molarity

Titration Id.	aliquot of acid	Vol. of 0.0103 M NaOH to neutralize	Molarity of Acid in Sample	Molarity Error +/- @ 1 s
1	20.00	9.95	0.0051	
2	40.00	19.65	0.0051	
3	40.00	19.80	0.0051	
Ave Molarity =			0.0051	0.00003

0.64%

Analyst/Date

rg Swoboda ---

6/21/01

**Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report**

**Client:** S. Bryan  
**RPL Numbers:** 01-01474 to 01-1475  
**Analyst:** MJ Steele

**Charge Code/Project:** W57955 / 42365  
**ASR Number:** 6140  
**Analysis Date:** August 27/28, 2001

**Procedure:** PNL-ALO-381, "Direct Determination of TC, TOC, and TIC in Radioactive Sludges and Liquids by Hot Persulfate Method"

**M&TE:** Carbon System (WA92040); Balance (360-06-01-023)

## Analysis Results

	Liquid Sample ID	TIC MDL µgC/mL	TIC Results µgC/mL	TIC RPD	TOC MDL µgC/mL	TOC Results µgC/mL	TOC RPD	TC Results µgC/mL	TC
RPL Number									
01-01474	AN-102-WS-Liquid	65	4,490		170	7,480		12,000	
01-01474 Dup	AN-102-WS-Liquid	65	4,420	2%	170	7,270	3%	11,700	2%
01-01474 MS	Recovery		97%			97%		97%	
Blank Spike/LCS	Recovery		99%			94%			

	Solids Sample ID	TIC MDL µgC/g	TIC Results µgC/g	TIC RPD	TOC MDL µgC/g	TOC Results µgC/g	TOC RPD	TC Results µgC/g	TC
RPL Number									
01-01475	AN-102-WS-10-Solid	110	3,520		300	27,900		31,400	
01-01475 Dup	AN-102-WS-10-Solid	58	3,890	10%	160	26,000	7%	29,900	5%
Batch MS (01-01631)	Recovery		96%			102%		100%	
Blank Spike/LCS	Recovery		100%			101%			

The TOC/TIC analyses of the samples submitted under ASRs 6164 are to be performed by both the hot persulfate and furnace methods. This report presents the results from the hot persulfate wet oxidation method. The hot persulfate method uses acid decomposition for TIC and acidic potassium persulfate oxidation at 92-95°C for TOC, all on the same sample, with TC being the sum of the TIC and TOC.

The table above shows the results, rounded to two to three significant figures. The raw data bench sheets and calculation work sheets showing all calculations are attached. All sample results are corrected for average percent recovery of system calibration standards and are also corrected for contribution from the blank, as per procedure PNL-ALO-381.

**Q.C. Comments:**

The TIC analysis uses calcium carbonate and the TOC uses  $\alpha$ -D-Glucose as the calibration, laboratory control, and matrix spike standards. (The JT Baker, Aldrich, Sigma, and Mallinckrodt chemical lot numbers and Chemical Measurement System numbers are provided on the raw data benchsheets).

The QC for the methods involves calibration blanks, sample duplicates, laboratory control sample, and matrix spikes per analysis batch (i.e., liquids and solids). The ASR indicates that the analyses are to be performed per the QA Plan “Conducting Analytical Work in Support of Regulatory Programs”; the performance of the QC samples is compared to this Plan.

## **Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report**

Laboratory Control Sample (LCS)/Blank Spike(BS): A LCS/BS was analyzed with each batch of samples. The LCS/BSs for both the liquid analysis and the solids analysis were within acceptance criteria of 80% to 120%.

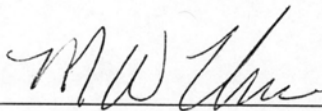
Matrix Spike: The accuracy of the carbon measurements can be estimated by the recovery results from the matrix spike. For the batch of liquid samples analyzed, sample AN-102-WS-10-Liquid was spiked with both TIC and TOC. For the batch of solids samples analyzed, the analysis batch matrix spike was performed on a solids sample from ASR 6164 (i.e., sample 01-01631). The matrix spikes demonstrate recoveries well within the acceptance criteria of 75% to 125% recovery.

Duplicates: The precision between the duplicates (replicates), as demonstrated by the Relative Percent Difference (RPD) between sample and duplicate. The TIC and TOC RPD results are well within the acceptance criteria of <20% RPD.

### **General Comments:**

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- Routine precision and bias are typically  $\pm 15\%$  or better for non-complex samples that are free of interferences.
- The estimated quantitation limit (EQL) is defined as 5 times the MDL. Results less than 5 times the MDL have higher uncertainties, and RPDs are not calculated for any results less than 5 times the MDL. The analysis MDLs (total ug C) are based on 3 times the standard deviation of a set of historical data. The sample MDLs (in ug C/ml or ug C/g) are calculated by using the analysis MDL adjusted for the sample volume or weight.
- Some results may be reported as less than ("<") values. These less than values represent the sample MDL (method detection limit), which is the system MDL adjusted for the volume of sample used for the analysis. The system MDL is based on the attached pooled historical blank data. The evaluation and calculation of the system MDL is included in the data package.

Report Prepared by: \_\_\_\_\_



Date 10-3-01

Review/Approval by: \_\_\_\_\_

Date \_\_\_\_\_

**Excel Archive File:** ASR 6140L&S 6155L 6164L&S.xls



PNNL Radiochemical Processing Group: TOC/TIC/TC Calculations \*\*Review\*\* Report - Hot Persulfate Method PNL-ALO-381

Client:	Burgeson/Bryan	Analyzer M&TE: WC01713 -- 701
Project :		Balance M&TE: 360-06-01-023
Work Pkg:	CMC	TOC STD: alpha-D-glucose Aldrich CMS#5329 40.00% Carbon <<[G]
Analyzed:	August 28, 2001	TIC STD: Calcium Carbonate Mallinkrodt CMS# 139285 11.99% Carbon <<[C]
ASR:	6164/6140	

		Raw TIC (ug C)	Raw TOC (ug C)	TIC	TOC		Is Blank Std Dev < Method Det Limit?
				12.3	51.0	<<< Blank Average (ug C)	
				1.5	3.0	<<< Blank Std Dev (ug C)	
Blanks:	Calibration blank (start of batch)	11.3	48.0	2.16	5.8	<<< Pooled Std Dev (ug C)	TIC Yes
	Calibration blank (start of batch)	11.5	51.0	6.5	17.3	<<< Method Det. Limit (ug C)	TOC Yes
	Calibration blank (end of batch)	14.0	54.0				

		Total Inorganic Carbon (TIC)				Total Organic Carbon (TOC)			
		[A] Raw TIC (ug)	[B] Blk (ug)	[D] Std wt (g)	TIC % Rec	[E] Raw TOC (ug)	[F] Blk (ug)	[H] Std wt (g)	TOC % Rec
Standards:	Calibration Standard (start of batch)	3158	12	0.0263	99.8	1843	51	0.0045	99.6
	Calibration Standard (start of batch)	3830	12	0.0320	99.5	1660	51	0.0041	98.1
	Calibration Standard (end of batch)	1600	12	0.0135	98.1	1075	51	0.0026	98.5
		[L] Average TIC % Rec >>>> 99.1				<<[P] Average TOC % Rec >>>> 98.7			
QC	Blank Spike/LCS	4882	12	0.0408	100.4	1645	51	0.0040	100.9
TOC	Sigma CMS#161713								
TIC	JT Baker CMS#161359								

Formulas:	Standard TIC % Recovery = $((A-B)/((C/100)*D))*10^{-6}*100$	Matrix Spike Recoveries:
	Standard TOC % Recovery = $((E-F)/((G/100)*H))*10^{-6}*100$	TIC % Recovery = $((Q-R)/(L/100))-S*T*100/U$
	Sample TIC (ug C/ml or ug C/g) = $(I-J)/(K*L/100)$	TOC % Recovery = $((Q-R)/(P/100))-S*T*100/U$
	Sample TOC (ug C/ml or ug C/g) = $(M-N)/(O*P/100)$	TC % Recovery = $((Q^{TIC}-R^{TIC})/(L/100))-V^{TIC}+(((Q^{TOC}-R^{TOC})/(P/100))-V^{TOC}))*100/U^{TIC+TOC}$
Comments:	Due to the precision carried in the spreadsheet, some results may appear to be slightly off due to rounding.	
	The Pooled SD is the averaged SD for a recent list of 12 sample batches. MDL is based upon the Pooled SD. MDL = 3 x pooled SD.	
	If either the Sample or Duplicate are < 5x mdl, then the RPD is not calculated and displayed as "n/a".	
	TIC and TOC are measured; TC is the sum of the TIC and TOC results.	

PNNL Radiochemical Processing Group: TOC/TIC/TC Calculations \*\*Review\*\* Report - Hot Persulfate Method PNL-ALO-381

Client:	Burgeson/Bryan	Analyzer M&TE:	WC01713 -- 701
Project :		Balance M&TE:	360-06-01-023
Work Pkg:	CMC	TOC STD: alpha-D-glucose Aldrich CMS#5329	40.00% Carbon <<[G]
Analyzed:	August 28, 2001	TIC STD: Calcium Carbonate Mallinkrodt CMS# 139285	11.99% Carbon <<[C]
ASR:	6164/6140		

Sample Results		Note: Sample weights are on "as received" basis; i.e., wet weight											
ACL Number	Client Sample ID	[I] Raw TIC (ug C)	[J] Blk (ug C)	[K] Sam wt (g)	TIC (ug C/g)	TIC RPD (%)	[M] Raw TOC (ug C)	[N] Blk (ug C)	[O] Sam wt (g)	TOC (ug C/g)	TOC RPD (%)	TC (ug C/g)	TC RPD (%)
ASR 6164													
01-01630	Caustic A	396	12	0.0341	11,354		993	51	0.03	27,986		39,340	
01-01630 Dup	Caustic A	693	12	0.0582	11,801	4	1404	51	0.06	23,551	17	35,352	11
01-01631	Caustic B	1444	12	0.1208	11,958		2952	51	0.12	24,329		36,287	
01-01631 MS	Caustic B	1948	12	0.1039	see below		3838	51	0.10	see below		see below	
ASR 6140													
01-01475	AN-102-WS-10-Solid	216	12	0.0584	3,520		1659	51	0.06	27,894		31,414	
01-01475 Dup	AN-102-WS-10-Solid	446	12	0.1124	3,893	10	2931	51	0.11	25,958	7	29,851	5

(Note: For any TOC or TIC result displayed as "# (<mdl)" the final reported "less than" concentration is calculated by dividing the Method Detection Limit by [K])

Matrix Spike Results		[Q] Raw MS (ug C)	[R] MS Blk (ug C)	[S] Sam (ug C/g)	[T] MS Sam wt (g)	[V] Sample (ug C)	Spike wt (g)	[U] Spike (ug C)	MS % Recovery
ACL Number	Client Sample ID								
01-01631 MS	TIC Recovery	1948	12	11958	0.1039	1242	0.0062	743	95.6 TIC
	TOC Recovery	3838	51	24329	0.1039	2528	0.0032	1280	102.2 TOC
	Total Carbon Recovery (TIC + TOC)							2023	99.8 TC

Reviewer/date: MW 10-02-01

## HOT PERSULFATE WORKSHEET

Client Burgess/Bryson ASR 6/14/140 Analyst M. Stille Date 8/28/01

Procedure: PNL-ALO-381 Analyzer M&TE: W C

Balance M&TE: 360-06-01-023

Standards:	TIC/CCV	TOC/BS/MS	TIC/CCV	TIC BS/MS
alpha-D-Glucose	alpha-D-Glucose	Calcium Carbonate	Calcium Carbonate	
Aldrich lot# HY12603EY	Sigma lot 58H01281	Mallinckrodt Lot# 4071	JT Baker Lot N30628	
solid - <del>Calcium carbonate</del>	solid	Solid - <del>Calcium carbonate</del>	solid	
CMS# 53219	CMS# 161713	CMS# 161732	CMS# 161359	

Lab ID	Client ID	volume	sample wt (g)	TIC (ug)	TOC (ug)	comments
Std 1	Blank 1			11.31	48	
	CCV 1	.0263	.0045	3158	1843	
Std 2	Blank 2			11.45	51	
	CCV 2	.0330	.0041	3830	1660	
	BS	.0408	.0040	4882	1645	
C1-1630	Caustic A		.0341	398	993	
Dup	↓		.0582	693	1404	
C1-1631	Caustic B		.1208	1444	2952	
MS	↓	.0062	.1039	1948	3838	
C1-1475	WS-10-501		.0884	216	1659	
Dup	↓		.1124	946	2931	
Blank 3				14	54	
Std 3	CCV 3	.0135	.0026	1600	1075	

Carbon Bench sheet.xls

PNNL Radiological Processing Group: TOC/TIC/TC Calculations \*\*Rev. \*\* Report - Hot Persulfate Method PNL-ALO-381

Client:	Burgeson/Arm/bryan
Project :	
Work Pkg:	CMC
Analyzed:	August 27, 2001
ASR:	6164/6155/6140

Analyzer M&TE:	WC01713 -- 701
Balance M&TE:	360-06-01-023
TOC STD:	alpha-D-glucose Aldrich CMS#5329 40.00% Carbon <<[G]
TIC STD:	Calcium Carbonate Mallinkrodt CMS# 139285 11.99% Carbon <<[C]

		Raw TIC (ug C)	Raw TOC (ug C)
Blanks:	Calibration blank (start of batch)	11.9	68.0
	Calibration blank (start of batch)	11.5	65.0
	Calibration blank (end of batch)	15.0	59.0

TIC	TOC	
12.8	64.0	<<< Blank Average (ug C)
1.9	4.6	<<< Blank Std Dev (ug C)
2.16	5.8	<<< Pooled Std Dev (ug C)
6.5	17.3	<<< Method Det. Limit (ug C)

Is Blank Std Dev <	
Method Det Limit?	Yes
TIC	Yes
TOC	Yes

		Total Inorganic Carbon (TIC)				Total Organic Carbon (TOC)			
		[A] Raw	[B]	[D] Std	TIC	[E] Raw	[F]	[H] Std	TOC
		TIC (ug)	Blk (ug)	wt (g)	% Rec	TOC (ug)	Blk (ug)	wt (g)	% Rec
Standards:	Calibration Standard (start of batch)	1543	13	0.0129	98.9	1690	64	0.0040	101.6
	Calibration Standard (start of batch)	1579	13	0.0132	99.0	1660	64	0.0038	105.0
	Calibration Standard	1701	13	0.0139	101.3	947	64	0.0022	100.3
	Calibration Standard (end of batch)	1570	13	0.0130	99.9	1040	64	0.0025	97.6
		[L] Average TIC % Rec >>>> 99.8 <<[L]				[P] Average TOC % Rec >>>> 101.1 <<[P]			
QC	Blank Spike/LCS	7657	13	0.0646	98.9	1090	64	0.0027	93.9
TOC	Sigma CMS#161713								
TIC	JT Baker CMS#161359								

Formulas:	Standard TIC % Recovery = $((A-B)/((C/100)*D))*10^{-6}*100$	Matrix Spike Recoveries:
	Standard TOC % Recovery = $((E-F)/((G/100)*H))*10^{-6}*100$	TIC % Recovery = $((Q-R)/(L/100))-S*T*100/U$
	Sample TIC (ug C/ml or ug C/g) = $(I-J)/(K*L/100)$	TOC % Recovery = $((Q-R)/(P/100))-S*T*100/U$
	Sample TOC (ug C/ml or ug C/g) = $(M-N)/(O*P/100)$	TC % Recovery = $((Q^{TIC}-R^{TIC})/(L/100))-V^{TIC}+(((Q^{TOC}-R^{TOC})/(P/100))-V^{TOC}))*100/U^{TIC+TOC}$
Comments:	Due to the precision carried in the spreadsheet, some results may appear to be slightly off due to rounding. The Pooled SD is the averaged SD for a recent list of 12 sample batches. MDL is based upon the Pooled SD. MDL = 3 x pooled SD. If either the Sample or Duplicate are < 5x mdl, then the RPD is not calculated and displayed as "n/a". TIC and TOC are measured; TC is the sum of the TIC and TOC results.	

PNNL Radiochemical Processing Group: TOC/TIC/TC Calculations \*\*Revised\*\* Report - Hot Persulfate Method PNL-ALO-381

Client:	Burgeson/Arm/bryan
Project :	
Work Pkg:	CMC
Analyzed:	August 27, 2001
ASR:	6164/6155/6140

	Analyzer M&TE: WC01713 -- 701
	Balance M&TE: 360-06-01-023
	TOC STD: alpha-D-glucose Aldrich CMS#5329 40.00% Carbon <<[G]
	TIC STD: Calcium Carbonate Mallinkrodt CMS# 139285 11.99% Carbon <<[C]

Sample Results		Note: Sample weights are on "as received" basis; i.e., wet weight											
		[I] Raw	[J]	[K] Sam	TIC	TIC	[M] Raw	[N]	[O] Sam	TOC	TOC	TC	TC
ACL Number	Client Sample ID (Liquids)	TIC (ug C)	Blk (ug C)	Vol (ml)	(ug C/ml)	RPD (%)	TOC (ug C)	Blk (ug C)	Vol (ml)	(ug C/ml)	RPD (%)	(ug C/ml)	RPD (%)
ASR 6164													
01-01624	AN102-15A	1246	13	0.10	12,360		2640	64	0.10	25,469		37,829	
01-01624 Dup	AN102-15A	1191	13	0.10	11,809	5	2665	64	0.10	25,716	1	37,525	1
01-01625	AN102-15B	1210	13	0.10	11,999		2801	64	0.10	27,061		39,060	
01-01626	AN102-50A	1210	13	0.10	11,999		2820	64	0.10	27,249		39,248	
01-01627	AN102-50B	1195	13	0.10	11,849		2758	64	0.10	26,636		38,485	
01-01628	AN102 Caustic A	1112	13	0.10	11,017		2771	64	0.10	26,764		37,782	
01-01629	AN102 Caustic B	1101	13	0.10	10,907		2669	64	0.10	25,756		36,663	
01-01629 MS	AN102 Caustic B	2797	13	0.10	see below		3780	64	0.10	see below		see below	
ASR 6155													
01-01593	MODAN105	148	13	0.10	1,355		362	64	0.10	2,946		4,302	
01-01593 Dup	MODAN105	1465	13	1.00	1,456	7	1200	64	1.00	1,123	90	2,579	50
ASR 6140													
01-01474	AN-102-WS-Liquid	461	13	0.10	4,492		820	64	0.10	7,475		11,967	
01-01474 Dup	AN-102-WS-Liquid	454	13	0.10	4,422	2	799	64	0.10	7,267	3	11,689	2
01-01474 MS	AN-102-WS-Liquid	2280	13	0.10	see below		2035	64	0.10	see below		see below	

(Note: For any TOC or TIC result displayed as "<[G]" the final reported "less than" concentration is calculated by dividing the Method Detection Limit by [K])

Matrix Spike Results		[Q] Raw MS	[R] MS Blk	[S] Sam	[T] MS Sam	[V] Sample	Spike	[U] Spike	MS
ACL Number	Client Sample ID	(ug C)	(ug C)	(ug C/ml)	Vol (ml)	(ug C)	wt (g)	(ug C)	% Recovery
01-01629 MS	TIC Recovery	2797	13	10907	0.10	1091	0.0140	1679	101.3
	TOC Recovery	3780	64	25756	0.10	2576	0.0027	1080	101.7
	Total Carbon Recovery (TIC + TOC)							2759	101.4
01-01474 MS	TIC Recovery	2280	13	4492	0.10	449	0.0157	1882	96.8
	TOC Recovery	2035	64	7475	0.10	747	0.0031	1240	96.9
	Total Carbon Recovery (TIC + TOC)							3122	96.9

Reviewer/date: *MW* 10-2-01

## HOT PERSULFATE WORKSHEET

Client Bayer/Am/Bayer ASR 6/6/11 Analyst M. Stule Date 8/27/11

Procedure: PNL-ALO-381 Analyzer M&TE: WC01113 Balance M&TE: 360-06-01-023 1g = 1,000

Standards: TIC CCV TIC BS/MS TIC CCV TIC BS/MS  
 alpha-D-Glucose alpha-D-Glucose Calcium Carbonate Calcium Carbonate  
 Aldrich lot# 1<sup>st</sup> 12603EY Sigma lot 58H01281 Mallinckrodt Lot# 4071 JT Baker Lot N30628  
 solid solid solid solid  
 CMS # 53219 CMS # 161713 CMS# 161359 CMS# 161359

Lab ID	Client ID	volume	sample wt (g)	TIC (ug)	TOC (ug)	comments
	Blank 1			11.85	6.8	liquids
	2			11.5	6.5	
Std 1	CCV 1	1ml DDE	0.029	947	1243	1543
Std 2	CCV 2	1ml DDE	0.132	1579	1660	1690
	BS	1ml DDE	0.046	7657	1090	11060
	01-1624	1ml		246	2640	0995
	Dup			1191	2665	1000
	01-1625			1210	2821	0988
	01-1626			1210	2820	0990
	01-1627			1195	2758	
	01-1628			1112	2771	
	01-1629			1101	2669	
	MS		0.027	2797	3780	
Std 3	CCV 3	1ml	0.031	1701	947	Blank 3 13.5 7.2
	01-1593	1ml		148	362	Small amount ppt
	Dup	1ml		1465	1200	Lots of ppt with persulfate (see std 1)
	01-1474	1ml		461	820	yellow solution
	Dup			454	799	
	MS		0.031	2280	2035	
Std 4	CCV 4		0.130	1570	1040	
	Blank 4			15	59	

Carbon Bench sheet.xls

**Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report**  
**PO Box 999, Richland, WA 99352**

**Client** S Bryan  
**RPL Numbers:** 01-1474 to 01-1475  
**Analyst:** MJ Steele

**Charge Code/Project:** W57955/ 42365  
**ASR Number:** 6140  
**Analysis Date:** 8/29 & 9/06, 2001

**Procedure:** PNL-ALO-380, "Determination of Carbon in Solids Using the Coulometrics Carbon Dioxide Coulometer"

**M&TE:** Carbon System (WD13071); Balance (360-06-01-023)

**TOC/TIC/TC Results**

RPL Number	Sample ID	TIC (a) MDL ugC/mL	TIC (b) Results ugC/mL	TOC MDL ugC/mL	TOC Results ugC/mL	TC MDL ugC/mL	TC Results ugC/mL
01-01474	AN-102-WS-Liquid	330	600	2,700	11,600	330	12,200
01-01474 Dup	AN-102-WS-Liquid	330	2,400	2,700	10,600	330	13,000
	RPD		n/a		9%		6%
	RSD		n/a		6%		5%
01-01627/29 MS <sup>(c)</sup>	Recovery				68%		104%
Blank Spike/LCS	Recovery				102%		101%
RPL Number	Sample ID	TIC (a) MDL ugC/g	TIC (b) Results ugC/g	TOC MDL ugC/g	TOC Results ugC/g	TC MDL ugC/g	TC Results ugC/g
01-01475	AN-102-WS-10-Solid	310	1,600	1,900	25,800	310	27,400
01-01475 Dup	AN-102-WS-10-Solid	480	1,600	1,100	27,500	480	29,100
	RPD		0%		7%		6%
	RSD		0%		5%		4%
01-01631 MS <sup>(c)</sup>	Recovery				81%		69%
Blank Spike/LCS	Recovery				102%		107%

n/a = not applicable (RPD not calculated, since results not >5x MDL)

(a) TIC MDL set to TC MDL

(b) TIC is determined by difference (TC - TOC)

(c) 01-01630 MS (solids) and 01-01627&01-01629 (liquids) are the analysis batch MS QC sample.

The TOC/TIC analyses of the samples submitted under ASR 6140 were to be performed by both the hot persulfate and furnace methods. This report presents the results from the furnace oxidation method and the results are compared to the results obtained from the hot persulfate method. Determination of total organic carbon (TOC) is performed by combusting an aliquot of the sample (solids or liquid) in oxygen at 750 °C for 30 minutes. The total carbon is determined on another aliquot of the sample by combusting at 1000 °C for 30 minutes. The total inorganic carbon is obtained by difference.

The table above shows the results, rounded to two to three significant figures. The raw data bench sheets and calculation work sheets showing all calculations are attached. All sample results are corrected for average percent recovery of system calibration standards and are also corrected for contribution from the blank, as per procedure PNL-ALO-380.



**Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report**  
**PO Box 999, Richland, WA 99352**

**Q.C. Comments:**

The calibration and QC standards for TC and TOC analysis are liquid or solid carbon standards or pure chemicals from JT Baker, Aldrich, Sigma, and Mallinckrodt. The identification of the standards and their Chemical Management System (CMS) numbers are included on the raw data benchsheets.

The coulometer analysis system calibration is checked by analyzing calibration standards at the beginning, middle, and end of each day's run. The average recovery from these calibration check standards is applied as a correction factor to the 'raw data' results obtained for the samples. The average recovery for the TOC was 100% and for TC was 99%.

System blanks were analyzed similarly to the calibration check, averaged, and subtracted from the sample 'raw data' results prior to calculating the final reported result. The TOC determination produced an average blank of 42 µgC and the TC determination produced an average blank of 37 µgC, which was subtracted from the sample measurements.

The QC for the analyses include sample duplicates, blank spikes (as a laboratory control sample), and matrix spikes. The ASR indicates that the analyses are to be performed per the QA Plan "Conducting Analytical Work in Support of Regulatory Programs", Sections 4 and 5.

Blank Spike/Laboratory Control Sample: The BS/LCS was within acceptance criteria of 80% to 120% required by governing QA Plan for both the TC and TOC analysis.

Duplicates: The precision between the duplicates (replicates), as demonstrated by the Relative Percent Difference (RPD), is acceptable for the samples. However, the TIC RPD for the liquid sample could not be calculated since both results were not at least 5 times the MDL.

Matrix Spike: The accuracy of the carbon measurements can be estimated by the recovery results from the matrix spike. The batch MS for TOC was 01-1629 for the liquid samples and 01-1630 for the solids samples, and the batch MS for TC was 01-1627 for the liquid samples and 01-1630 for the solids samples. The TOC for the liquids and the TC for the solids failed to meet the acceptance criteria of 75% to 125% recovery. Since there is no indication of system failure (i.e., all other QC samples meet criteria), the low MS recovery is most likely an unknown matrix effect.

**Furnace Results Compared to Hot Persulfate Results**

RPL Number	Sample ID	TIC HP Results ugC/mL	TIC Furn Results <sup>(a)</sup> ugC/mL	TOC HP Results ugC/mL	TOC Furn Results ugC/mL	TC HP Results <sup>(b)</sup> ugC/mL	TC Furn Results ugC/mL
01-01474	AN-102-WS-Liquid	4,490	600	7,480	11,600	12,000	12,200
RPL Number	Sample ID	TIC HP Results ugC/g	TIC Furn Results <sup>(a)</sup> ugC/g	TOC HP Results ugC/g	TOC Furn Results ugC/g	TC HP Results <sup>(b)</sup> ugC/g	TC Furn Results ugC/g
01-01475	AN-102-WS-10-Solid	3,520	1,600	27,900	25,800	31,400	27,400
a) TIC Furn is determined by difference (TC - TOC)							
b) TC HP is determined by sum (TIC + TOC)							



**Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report**  
**PO Box 999, Richland, WA 99352**

The two methods appear to produce comparable results for TC for the liquid samples. However, there are significant differences between the TIC and TOC results from some samples. The reason for the discrepancy between the hot persulfate method and furnace method is unknown. Typically, the furnace method provides the best TC results and the hot persulfate the best TIC results, thus the TOC would be the difference between these measurements (i.e., a result closer to the hot persulfate TOC than the furnace TOC.)

For the solids samples, the same trend is observed. However, the lower furnace TC result compared to the hot persulfate TC results is unusual.

**General Comments:**

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- Routine precision and bias are typically  $\pm 15\%$  or better for non-complex samples that are free of interferences.
- For both the TC and TOC, the analysis Method Detection Limit (MDL) is based on the standard deviation calculated from the number (n) of system blanks analyzed with the batch of samples. The standard deviation is multiplied by the Student's *t* values for *n*-1 degrees of freedom to establish the daily MDL. The sample MDL (in ug C/ml or ug C/g) are calculated by using the analysis MDL adjusted for the sample volume or weight.
- Some results may be reported as less than (" $<$ ") values. These less than values represent the sample MDL (method detection limit), which is the system MDL adjusted for the volume of sample used for the analysis.
- The estimated quantitation limit (EQL) is defined as 5 times the MDL. Results less than 5 times the MDL have higher uncertainties, and RPDs are not calculated for any results less than 5 times the MDL.

Report Prepared by:

MW Han

Date 12-19-01

Review/Approval by:

MJ Steele

Date 1-3-02

Raw Data Calculation/Archive Information: ASR 6140 6155 6164.xls



Project No. 42365

Internal Distribution  
File/LB

Date February 1, 2002  
To Sam Bryan  
From Karl Pool *Karl N. Pool 2/1/02*  
Subject Wt % Solids/TDS analysis

Sam,

Attached are the bench sheet results for the Wt.% Solids/TDS analyses of two AN-102 samples submitted with ASR 6140. The samples were analyzed in accordance with PNL analytical procedure PNL-ALO-504. The PNNL analytical procedure was performed within the Hot Cells of the 325 laboratory. All samples were weighed using a Mettler AE160 balance (M&TE # 360-06-01-016) located in Hot Cell number two of the Shielded Analytical Laboratory. All temperature readings were obtained from a calibrated thermocouple (M&TE # 3118) and temperature readout (M&TE # 2115). All samples were performed in duplicate. The samples have been assigned RPL log numbers 01-01474 and 01-01475. Work package number W57955 will be charged for the analyses.

WT% SOLIDS/TDS DATA SHEET  
(325 SHIELDED ANALYTICAL LABORATORY)

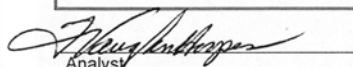
CLIENT: Sam Bryan WORK PACKAGE: W57955 ASR/ARF/LOI/TI: 6140  
QA PLAN: HASQARD PROJECT NUMBER: 42365 PROCEDURE NO.: PNL-ALO-504

AN-102-WS-10 Liquid and Solid  
SAMPLE IDENTIFICATION

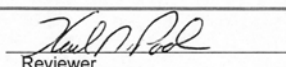
ACL NUMBER	CLIENT IDENTIFICATION	TARE WEIGHT (g)	(A) SAMPLE WET WEIGHT PLUS TARE	(B) SAMPLE DRY WEIGHT PLUS TARE	WEIGHT % SOLIDS/TDS
01-01474	AN-102-WS-10 Liq.	8.1216	8.6602	8.2078	16.00% TDS
01-01474-Dup	AN-102-WS-10 Liq.-Dup	8.0893	8.6322	8.1764	16.04% TDS
01-01475	AN-102-WS-10 Sol.	8.1611	9.8897	8.9248	44.18% Solids
01-01475 -Dup	AN-102-WS-10 Sol.-Dup	8.1504	9.8286	8.9029	44.84% Solids

WT% SOLIDS =  $\frac{B - TARE}{A - TARE} \times 100$  DATE/TIME IN: 7/5/01 13:30 OVEN TEMPERATURE: 104 °C  
DATE/TIME OUT: 7/6/01 10:00 OVEN TEMPERATURE: 107 °C  
BALANCE : CELL 2 (360-06-01-016) X

TEMPERATURE READOUT: 2115 Expiration Date: 5/02  
THERMOCOUPLE: 3118 Expiration Date: 4/02

  
Analyst

7-9-01  
Date

  
Reviewer

7/9/01  
Date

# FINAL REPORT

The attached report is sent for **final distribution** to the client.

Status these tests as sent to client -

ACL Numbers: 01-1474, 1475

ASR Number: 6140

Tests: Ta, T<sub>β</sub>, Am/Cm, 90Sr, GEA

File in Project File -

Project Number: 42365 or ED Work Order: \_\_\_\_\_

or ☐ ACL Waste File, or P.E. File: \_\_\_\_\_

Distribution -

	Send				
	B	R		S	
	Y	E		U	
		P	D	P	
	F	O	A	O	
	A	R	T	R	
Send To	X	T	A	T	MSIN, Address, Fax Number (as req'd)
<u>Sam Bryan</u>		<u>X</u>			

☐ Special distribution instructions are attached.

Project Manager -

Signature: J. Greenwood Date: 9-25-01

Return copy of this coversheet to: \_\_\_\_\_

For LSO Use Only

Sent to client by: Karla Smith Date: 9/26/01

**Battelle Pacific Northwest Laboratory**  
Radiochemical Processing Group-325 Building  
Radioanalytical Applications Team

01-1474

9/13/01

Client : Sam Bryan

Cognizant Scientist:

JR Greenwood

Date :

9/25/01

Concur :

T Trang - 6

Date :

9/13/01

Measured Activities (uCi/g) with 1-sigma error

ALO ID Client ID	Beta Error +/-	Sr-90 Error +/-	Co-60 Error %	Cs-137 Error %	Eu-154 Error %	Eu-155 Error %	Am-241 Error %
01-1474 PB Process Blank	2.06E-2 4%	1.01E-2 4%	<2.E-4	1.61E-3 5%	<4.E-4	<4.E-4	<3.E-4
01-1474 AN-102-WS-10-Liquid	8.19E+1 4%	5.96E+0 3%	1.72E-2 7%	6.88E+1 2%	<2.E-2	<7.E-2	<6.E-2
01-1474 DUP AN-102-WS-10-Liquid	8.11E+1 4%	6.53E+0 3%	1.62E-2 8%	6.85E+1 2%	<2.E-2	<7.E-2	<6.E-2
RPD	1%	9%	6%	0%			
01-1475PB Process Blank	4.27E-1 4%	2.27E-1 3%	<2.E-4	9.40E-3 3%	<4.E-4	<6.E-4	<2.E-3
01-1475 AN-102-WS-10- Solids	2.14E+3 3%	1.06E+3 3%	5.56E-2 7%	1.08E+2 3%	2.93E+0 2%	1.73E+0 5%	2.92E+0 6%
01-1475 DUP AN-102-WS-10- Solids	2.03E+3 4%	1.03E+3 3%	5.16E-2 7%	1.11E+2 3%	2.92E+0 2%	1.86E+0 5%	2.98E+0 6%
RPD	5%	3%	7%	3%	0%	7%	2%
Matrix Spike	99%	95%					
Blank Spike	97%	101%					
Blank	1.00E-4 33%	<3.E-4					

**Battelle Pacific Northwest Laboratory**  
Radiochemical Processing Group-325 Building  
Radioanalytical Applications Team

01-1474

09/25/01

Client : Sam Bryan

Cognizant Scientist:

LR Gernard Date : 9/25/01

Concur :

T Trang-k Date : 9/25/01

Measured Activities (uCi/g) with 1-sigma error

ALO ID Client ID	Alpha Error +/-	Am-241 Error +/-	Cm-243+ Cm-244 Error +/-	Cm-242 Error +/-	Sum of Alpha Error +/-
01-1474 PB Process Blank	9.68E-5 16%	3.07E-5 8%	1.53E-5 11%	<1.E-6	4.70E-5 6%
01-1474 AN-102-WS-10-Liquid	1.81E-2 12%	1.42E-2 2%	6.07E-4 6%	5.85E-5 18%	1.49E-2 2%
01-1474 DUP AN-102-WS-10-Liquid	1.80E-2 12%	1.40E-2 2%	5.87E-4 4%	4.05E-5 15%	1.46E-2 2%
RPD	1%	1%	3%	36%	2%
01-1475PB Process Blank	<1E-4	4.25E-5 11%	1.59E-5 16%	<2.E-6	6.04E-5 9%
01-1475 AN-102-WS-10- Solids	3.38E+0 2%	2.46E+0 2%	8.90E-2 6%	8.19E-3 19%	2.56E+0 2%
01-1475 DUP AN-102-WS-10- Solids	3.17E+0 2%	2.48E+0 2%	8.16E-2 6%	4.29E-3 24%	2.57E+0 2%
RPD	6%	1%	9%	63%	0%
Matrix Spike	113%	92%			
Blank Spike	102%	93%			
Blank	<5.E-5	<2.E-6	<6.E-7	<6.E-7	

# FINAL REPORT

The attached report is sent for **final distribution** to the client.

Status these tests as sent to client -

ACL Numbers: 01474, 1975

ASR Number: 6140

Tests: GEA - Revised Report

File in Project File -

Project Number: 42305 or ED Work Order: \_\_\_\_\_

or    ACL Waste File, or P.E. File: \_\_\_\_\_

Distribution -

	Send				
	B	R		S	
	Y	E		U	
		P	D	P	
	F	O	A	O	
	A	R	T	R	
Send To	X	T	A	T	MSIN, Address, Fax Number (as req'd)
<u>Sam Bryan</u>	<u>X</u>				
_____					
_____					
_____					
_____					
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_____					

   Special distribution instructions are attached.

Project Manager -

Signature: L. Greenwood Date: 9-27-01

Return copy of this coversheet to: \_\_\_\_\_

For LSO Use Only

Sent to client by: Karee Smith Date: 9/28/01



Date September 27, 2001  
To S. A. Bryan  
From L. R. Greenwood *LRG*  
Subject Radiochemical Analyses for AN-102 -ASR 6140

Samples WS-10 of the supernates and solids from tank AN-102 were analyzed for total alpha, total beta, gamma,  $^{90}\text{Sr}$ , Pu, and Am/Cm activities according to ASR 6140. The samples were acid digested in the hot cells according to procedures PNL-ALO-128 (liquids) and -129 (solids) and aliquots were delivered to the laboratory for analysis. The attached reports list measured analyte activities in the original sample material in units of  $\mu\text{Ci/g}$  for both the supernates and the solids since densities were not known for the supernates. The 1- $\sigma$  total propagated uncertainties are reported including counting, dilution, yield, and calibration errors, as appropriate. Laboratory and process blank values given with each analysis are the best indicators of the method detection limits, taking into account the actual sample sizes and counting times used for each analysis.

The hot cell sample preparations were performed in two separate batches for the supernates and solids. However, all of the samples were analyzed together in one batch in the laboratory.

### Gamma Spectrometry

Sample aliquots were directly counted for gamma emitters according to procedure PNL-ALO-450. Since no sample preparation was involved, no laboratory blanks or spikes were prepared for these analyses other than the standard laboratory control samples and background counts. All of the samples showed the presence of  $^{137}\text{Cs}$  activity with smaller amounts of  $^{60}\text{Co}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$ , and  $^{241}\text{Am}$  in the solids. The MRQ values for extended counting time GEA were met in all cases. Only negligible activities were seen in the hot cell process blanks. Sample duplicates were in good agreement.

### Gross Alpha and Beta

The gross alpha and beta analyses were performed according to procedure RPG-CMC-408. In both cases, direct aliquots of the sample digestions from the hot cells were dried on counting plates. The beta activity was determined with a gas proportional counter and the alpha activity was measured with a ZnS scintillation counter. For both analyses, the activities in the hot cell and laboratory blanks were negligible. Matrix spikes and blank spikes showed acceptable recovery between 97-113%. For the gross beta measurements, the measured activities are in good agreement with the sum of the major beta emitters, namely  $^{90}\text{Sr}$  (x 2 for  $^{90}\text{Y}$ ) plus  $^{137}\text{Cs}$ . For the gross alpha measurements, the measured activities uniformly exceed the sum of the alpha emitters, which is



given in the far right column on the table. This difference is most likely explained by the presence of Pu in the samples.

#### **Americium and Curium**

The Am/Cm separations were performed sequentially according to PNL-ALO-417. The separated fractions were precipitation plated according to PNL-ALO-496 and the samples were counted by alpha spectrometry according to PNL-ALO-422. The curium is known to follow the americium and both these isotopes were traced with  $^{243}\text{Am}$ . The americium recovery for the blank spike was 93% and the matrix spike recovery was 92%. Neither Am or Cm were detected in the laboratory preparation blank and these activities were negligible in the hot cell process blanks. Sample duplicates were in acceptable agreement taking into account the counting uncertainties. All of the sample and blank activities met the requested MRQ values.

#### **Strontium-90**

The Sr separation was performed according to PNL-ALO-476. Radiochemical yields were traced with  $^{85}\text{Sr}$ . The separated fractions were then beta-counted according to RPG-CMC-408 and gamma counted according to PNL-ALO-450 (for  $^{85}\text{Sr}$  determination and  $^{137}\text{Cs}$  impurity assessment). No  $^{90}\text{Sr}$  was found in the laboratory preparation blank and the activities in the hot cell process blanks were negligible. The RPD for the sample duplicates were 1% and 5% for the supernates and solids, respectively. The LCS and matrix spike recoveries were 101% and 95%, respectively. The activities in the samples were well above the requested MRQ values.

**Battelle Pacific Northwest Laboratory**  
Radiochemical Processing Group-325 Building  
Radioanalytical Applications Team

01-1474

09/27/01

Client : Sam Bryan

Cognizant Scientist:

*L. R. Greenwood*

Date :

*9/27/01*

Concur :

*T. Trang-le*

Date :

*9/27/01*

Measured Activities (uCi/g) with 1-sigma error

ALO ID Client ID	Beta Error +/-	Sr-90 Error +/-	Co-60 Error %	Cs-137 Error %	Eu-154 Error %	Eu-155 Error %	Am-241 Error %
01-1474 PB Process Blank	2.06E-2 4%	1.01E-2 4%	<2.E-4	1.61E-3 5%	<4.E-4	<4.E-4	<3.E-4
01-1474 AN-102-WS-10-Liquid	8.19E+1 4%	5.96E+0 3%	1.68E-2 3%	6.25E+1 3%	2.18E-2 5%	<7.E-2	<6.E-2
01-1474 DUP AN-102-WS-10-Liquid	8.11E+1 4%	6.53E+0 3%	1.70E-2 4%	6.46E+1 3%	2.37E-2 7%	<3.E-2	<1.E-2
RPD	1%	9%	1%	3%	8%		
01-1475PB Process Blank	4.27E-1 4%	2.27E-1 3%	<2.E-4	9.40E-3 3%	<4.E-4	<6.E-4	<2.E-3
01-1475 AN-102-WS-10- Solids	2.14E+3 3%	1.06E+3 3%	5.56E-2 7%	1.08E+2 3%	2.93E+0 2%	1.73E+0 5%	2.92E+0 6%
01-1475 DUP AN-102-WS-10- Solids	2.03E+3 4%	1.03E+3 3%	5.16E-2 7%	1.11E+2 3%	2.92E+0 2%	1.86E+0 5%	2.98E+0 6%
RPD	5%	3%	7%	3%	0%	7%	2%
Matrix Spike	99%	95%					
Blank Spike	97%	101%					
Blank	1.00E-4 33%	<3.E-4					



Thm-1

Project No. \_\_\_\_\_

Internal Distribution

File/LB

Date July 12, 2001

To S.A. Bryan

From S.J. Bos

*Stan Bos*

Subject Gas sample analyses

Analyses of ten 23HC50 samples received July 9, 2001 have been completed. A report detailing the analyses is attached. Sample analyses were performed on the Finnigan MAT-271 (M&TE WC38625) quantitative gas mass spectrometer. A performance check of the instrument is run daily, prior to running samples, using high purity nitrogen. Two weekly air standards are also analyzed to ensure the instrument is functioning properly. The RPL numbers for the samples are 01-01597 through 01-01606. Work package W57955 will be charged for the analyses.

If you have any questions please call me on 376-3358 or 376-5384.

Concurrence:

*MW Golea*

7-19-01

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: July 11, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 114  
Measurement and test equipment WC38625

Sample ID: 23HC50-1  
Analysis Date: July 10, 2001  
RPL Number: 01-01597

Mole  
Percent Estimate of  
Precision

Argon	0.004 ± 0.001
Carbon Dioxide	0.064 ± 0.001
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.022 ± 0.001
Methane	< 0.001 ± 0
Nitrogen	0.274 ± 0.005
Oxygen	0.022 ± 0.001
Nitrous Oxide	0.046 ± 0.001
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	99.57 ± 0.05
Comments:	

Sample ID: 23HC50-2  
Analysis Date: July 10, 2001  
RPL Number: 01-01598

Mole  
Percent Estimate of  
Precision

Argon	0.003 ± 0.0005
Carbon Dioxide	0.018 ± 0.001
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.031 ± 0.001
Methane	< 0.001 ± 0
Nitrogen	0.225 ± 0.005
Oxygen	0.007 ± 0.001
Nitrous Oxide	0.064 ± 0.001
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	99.65 ± 0.05
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: July 11, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 114  
Measurement and test equipment WC38625

Sample ID: 23HC50-3 ✓  
Analysis Date: July 10, 2001  
RPL Number: 01-01599

	Mole Percent	Estimate of Precision
Argon	0.003	± 0.0005
Carbon Dioxide	0.021	± 0.001
Carbon Monoxide	< 0.01	± 0
Helium	0.005	± 0.001
Hydrogen	0.029	± 0.001
Methane	< 0.001	± 0
Nitrogen	0.307	± 0.006
Oxygen	0.045	± 0.001
Nitrous Oxide	0.062	± 0.001
Other Nitrogen Oxides	< 0.005	± 0
C2Hx	< 0.001	± 0
Other Hydrocarbons	< 0.001	± 0
Ammonia (estimated)		± 0
Neon	99.53	± 0.05
Comments:		

Sample ID: 23HC50-4 ✓  
Analysis Date: July 10, 2001  
RPL Number: 01-01600

	Mole Percent	Estimate of Precision
Argon	0.66	± 0.01
Carbon Dioxide	0.03	± 0.001
Carbon Monoxide	< 0.01	± 0
Helium	< 0.001	± 0
Hydrogen	0.009	± 0.001
Methane	< 0.001	± 0
Nitrogen	54.9	± 0.7
Oxygen	14.8	± 0.3
Nitrous Oxide	0.02	± 0.001
Other Nitrogen Oxides	< 0.005	± 0
C2Hx	< 0.001	± 0
Other Hydrocarbons	< 0.001	± 0
Ammonia (estimated)		± 0
Neon	29.6	± 0.6
Comments: Sample cylinder valve was leaking.		

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: July 11, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 115  
Measurement and test equipment WC38625

Sample ID: 23HC50-5  
Analysis Date: July 10, 2001  
RPL Number: 01-01601

	Mole Percent	Estimate of Precision
Argon	0.002 ± 0.0005	
Carbon Dioxide	0.021 ± 0.001	
Carbon Monoxide	< 0.01 ± 0	
Helium	< 0.001 ± 0	
Hydrogen	0.056 ± 0.001	
Methane	< 0.001 ± 0	
Nitrogen	0.333 ± 0.007	
Oxygen	0.038 ± 0.001	
Nitrous Oxide	0.164 ± 0.001	
Other Nitrogen Oxides	< 0.005 ± 0	
C2Hx	< 0.001 ± 0	
Other Hydrocarbons	< 0.001 ± 0	
Ammonia (estimated)	± 0	
Neon	99.39 ± 0.05	
Comments:		

Sample ID: 23HC50-6  
Analysis Date: July 10, 2001  
RPL Number: 01-01602

	Mole Percent	Estimate of Precision
Argon	0.002 ± 0.0005	
Carbon Dioxide	0.021 ± 0.001	
Carbon Monoxide	< 0.01 ± 0	
Helium	< 0.001 ± 0	
Hydrogen	0.056 ± 0.001	
Methane	0.002 ± 0.0005	
Nitrogen	0.289 ± 0.006	
Oxygen	0.033 ± 0.001	
Nitrous Oxide	0.179 ± 0.001	
Other Nitrogen Oxides	< 0.005 ± 0	
C2Hx	< 0.001 ± 0	
Other Hydrocarbons	< 0.001 ± 0	
Ammonia (estimated)	± 0	
Neon	99.42 ± 0.05	
Comments:		

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: July 11, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 115  
Measurement and test equipment WC38625

Sample ID: 23HC50-7  
Analysis Date: July 10, 2001  
RPL Number: 01-01603

Mole  
Percent Estimate of  
Precision

Argon	0.005 ± 0.001
Carbon Dioxide	0.024 ± 0.001
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.090 ± 0.002
Methane	0.002 ± 0.0005
Nitrogen	0.61 ± 0.01
Oxygen	0.028 ± 0.001
Nitrous Oxide	0.85 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	0.002 ± 0.0005
Other Hydrocarbons	0.001 ± 0.0005
Ammonia (estimated)	± 0
Neon	98.39 ± 0
Comments:	

Sample ID: 23HC50-8  
Analysis Date: July 10, 2001  
RPL Number: 01-01604

Mole  
Percent Estimate of  
Precision

Argon	0.003 ± 0.001
Carbon Dioxide	0.014 ± 0.001
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.104 ± 0.002
Methane	0.001 ± 0.0005
Nitrogen	0.43 ± 0.01
Oxygen	0.044 ± 0.001
Nitrous Oxide	0.81 ± 0.02
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	0.003 ± 0.001
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.59 ± 0.05
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: July 11, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 115  
Measurement and test equipment WC38625

Sample ID: 23HC50-9  
Analysis Date: July 10, 2001  
RPL Number: 01-01605

✓  
Mole  
Percent  
Estimate of  
Precision

Argon	0.003 ± 0.001
Carbon Dioxide	<0.1 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.236 ± 0.005
Methane	0.006 ± 0.001
Nitrogen	1.19 ± 0.03
Oxygen	0.038 ± 0.001
Nitrous Oxide	2.7 ± 0.1
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	0.006 ± 0.001
Other Hydrocarbons	0.001 ± 0.0005
Ammonia (estimated)	± 0
Neon	95.8 ± 0.1
Comments:	

Sample ID: 23HC50-10  
Analysis Date: July 10, 2001  
RPL Number: 01-01606

✓  
Mole  
Percent  
Estimate of  
Precision

Argon	0.003 ± 0.001
Carbon Dioxide	<0.1 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	0.005 ± 0.001
Hydrogen	0.214 ± 0.004
Methane	0.008 ± 0.001
Nitrogen	1.18 ± 0.03
Oxygen	0.037 ± 0.001
Nitrous Oxide	3.0 ± 0.1
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	0.006 ± 0.001
Other Hydrocarbons	0.001 ± 0.0005
Ammonia (estimated)	± 0
Neon	95.6 ± 0.1
Comments:	



## Pacific Northwest National Laboratory

From: 325 Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-3358 / mail slot P7-22  
Date: July 09, 2001  
Subject: Air standards from Finnigan MAT - 271 Mass Spectrometer

Analytical procedure: PNNL - 98523 - 284 Rev. 0  
Laboratory Record Book 56998: Page 114  
Measurement and test equipment WC38625

Accepted values for the composition of air :

	Mole percent
Argon	0.934
Nitrogen	78.08
Oxygen	20.95

Analyzed Values:

Analysis Date: July 09,2001

	Mole percent
Argon	0.939
Nitrogen	78.09
Oxygen	20.93

Analyzed Values:

Analysis Date: July 09,2001

	Mole percent
Argon	0.937
Nitrogen	77.91
Oxygen	21.11

Instrument Background:

Background analyses are run daily prior to sample analyses. Trace amounts of hydrogen and/or water in the 0.1 to 0.2 millivolt range were the only species detected. The background spectra is subtracted from each sample spectra.



Project No. \_\_\_\_\_

Internal Distribution

File/LB

Date October 11, 2001

To S.A. Bryan

From S.J. Bos *Stan Bos*

Subject Gas sample analyses

Corrected Report:

Neon results were left off the original report. The attached corrected report includes the Ne results.

(Analyses of ten 23HC56 samples received July 25, 2001 have been completed. A report detailing the analyses is attached. Sample analyses were performed on the Finnigan MAT-271 (M&TE WC38625) quantitative gas mass spectrometer. A performance check of the instrument is run daily, prior to running samples, using high purity nitrogen. Two weekly air standards are also analyzed to ensure the instrument is functioning properly. The RPL numbers for the samples are 01-01771 through 01-01780. Work package W57955 will be charged for the analyses.)

If you have any questions please call me on 376-3358 or 376-5384.

Concurrence:

*W. M. Moley 10-11-01*

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: August 4, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 116  
Measurement and test equipment WC38625

Sample ID:	23HC56-1		
Analysis Date:	July 26, 2001	Mole	Estimate of
RPL Number:	01-01771	Percent	Precision
Argon		0.002	± 0.0005
Carbon Dioxide		0.063	± 0.001
Carbon Monoxide		< 0.01	± 0
Helium		< 0.001	± 0
Hydrogen		0.028	± 0.001
Methane		< 0.001	± 0
Nitrogen		0.167	± 0.003
Oxygen		0.016	± 0.001
Nitrous Oxide		0.054	± 0.001
Other Nitrogen Oxides		< 0.005	± 0
C2Hx		< 0.001	± 0
Other Hydrocarbons		< 0.001	± 0
Ammonia (estimated)			± 0
Neon		99.67	± 0.05
Comments:			

Sample ID:	23HC56-2		
Analysis Date:	July 26, 2001	Mole	Estimate of
RPL Number:	01-01772	Percent	Precision
Argon		0.002	± 0.0005
Carbon Dioxide		0.009	± 0.001
Carbon Monoxide		< 0.01	± 0
Helium		< 0.001	± 0
Hydrogen		0.037	± 0.001
Methane		< 0.001	± 0
Nitrogen		0.156	± 0.003
Oxygen		0.011	± 0.001
Nitrous Oxide		0.069	± 0.001
Other Nitrogen Oxides		< 0.005	± 0
C2Hx		< 0.001	± 0
Other Hydrocarbons		< 0.001	± 0
Ammonia (estimated)			± 0
Neon		99.72	± 0.05
Comments:			

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: August 4, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 569980 Page 116  
Measurement and test equipment WC38625

Sample ID:	23HC56-3	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01773		
Argon	0.003 ± 0.001		
Carbon Dioxide	0.005 ± 0.001		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.034 ± 0.001		
Methane	< 0.001 ± 0		
Nitrogen	0.301 ± 0.006		
Oxygen	0.040 ± 0.001		
Nitrous Oxide	0.050 ± 0.001		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	< 0.001 ± 0		
Ammonia (estimated)	± 0		
Neon	99.57 ± 0.05		
Comments:			

Sample ID:	23HC56-4	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01774		
Argon	0.002 ± 0.001		
Carbon Dioxide	0.008 ± 0.001		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.041 ± 0.001		
Methane	< 0.001 ± 0		
Nitrogen	0.172 ± 0.003		
Oxygen	0.025 ± 0.001		
Nitrous Oxide	0.065 ± 0.001		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	< 0.001 ± 0		
Ammonia (estimated)	± 0		
Neon	99.69 ± 0.05		
Comments:			

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: August 4, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 569980 Page 116  
Measurement and test equipment WC38625

Sample ID:	23HC56-5		
Analysis Date:	July 26, 2001	Mole	Estimate of
RPL Number:	01-01775	Percent	Precision
Argon	0.002	±	0.0005
Carbon Dioxide	0.017	±	0.001
Carbon Monoxide	< 0.01	±	0
Helium	< 0.001	±	0
Hydrogen	0.054	±	0.001
Methane	< 0.001	±	0
Nitrogen	0.250	±	0.005
Oxygen	0.021	±	0.001
Nitrous Oxide	0.252	±	0.005
Other Nitrogen Oxides	< 0.005	±	0
C2Hx	< 0.001	±	0
Other Hydrocarbons	< 0.001	±	0
Ammonia (estimated)		±	0
Neon	99.41	±	0.05
Comments:			

Sample ID:	23HC56-6		
Analysis Date:	July 26, 2001	Mole	Estimate of
RPL Number:	01-01776	Percent	Precision
Argon	< 0.001	±	0
Carbon Dioxide	0.015	±	0.001
Carbon Monoxide	< 0.01	±	0
Helium	< 0.001	±	0
Hydrogen	0.060	±	0.001
Methane	< 0.001	±	0
Nitrogen	0.190	±	0.003
Oxygen	0.018	±	0.001
Nitrous Oxide	0.249	±	0.005
Other Nitrogen Oxides	< 0.005	±	0
C2Hx	< 0.001	±	0
Other Hydrocarbons	< 0.001	±	0
Ammonia (estimated)		±	0
Neon	99.47	±	0.05
Comments:			

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: August 4, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 569980 Page 116  
Measurement and test equipment WC38625

Sample ID:	23HC56-7	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01777		
Argon	0.003 ± 0.001		
Carbon Dioxide	<0.1 ± 0		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.071 ± 0.001		
Methane	0.002 ± 0.001		
Nitrogen	0.390 ± 0.008		
Oxygen	0.014 ± 0.001		
Nitrous Oxide	0.95 ± 0.02		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	0.001 ± 0.0005		
Ammonia (estimated)	± 0		
Neon	98.6 ± 0.1		
Comments:			

Sample ID:	23HC56-8	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01778		
Argon	0.011 ± 0.001		
Carbon Dioxide	<0.1 ± 0		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.088 ± 0.002		
Methane	< 0.001 ± 0		
Nitrogen	1.31 ± 0.03		
Oxygen	0.163 ± 0.003		
Nitrous Oxide	0.96 ± 0.02		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	< 0.001 ± 0		
Ammonia (estimated)	± 0		
Neon	97.5 ± 0.1		
Comments:			

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: August 4, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 117  
Measurement and test equipment WC38625

Sample ID:	23HC56-9	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01779		
Argon	0.001	± 0.0005	
Carbon Dioxide	<0.1	± 0	
Carbon Monoxide	< 0.01	± 0	
Helium	< 0.001	± 0	
Hydrogen	0.169	± 0.003	
Methane	0.007	± 0.001	
Nitrogen	0.96	± 0.2	
Oxygen	0.026	± 0.001	
Nitrous Oxide	2.4	± 0	
Other Nitrogen Oxides	< 0.005	± 0	
C2Hx	< 0.001	± 0	
Other Hydrocarbons	< 0.001	± 0	
Ammonia (estimated)		± 0	
Neon	96.4	± 0.1	
Comments:			

Sample ID:	23HC56-10	Mole	Estimate of
Analysis Date:	July 26, 2001	Percent	Precision
RPL Number:	01-01780		
Argon	0.001	± 0.0005	
Carbon Dioxide	< 0.1	± 0	
Carbon Monoxide	< 0.01	± 0	
Helium	< 0.001	± 0	
Hydrogen	0.147	± 0.003	
Methane	0.009	± 0.001	
Nitrogen	0.89	± 0.02	
Oxygen	0.022	± 0.001	
Nitrous Oxide	2.7	± 0.05	
Other Nitrogen Oxides	< 0.005	± 0	
C2Hx	< 0.001	± 0	
Other Hydrocarbons	0.001	± 0.0005	
Ammonia (estimated)		± 0	
Neon	96.3	± 0.1	
Comments:			





8-1

Project No. \_\_\_\_\_

Internal Distribution

File/LB

Date September 26, 2001

To S.A. Bryan

From S.J. Bos *S. J. Bos*

Subject Gas sample analyses

Analyses of ten 23HC64 samples received September 25, 2001 have been completed. A report detailing the analyses is attached. Sample analyses were performed on the Finnigan MAT-271 (M&TE WC38625) quantitative gas mass spectrometer. A performance check of the instrument is run daily, prior to running samples, using high purity nitrogen. Two weekly air standards are also analyzed to ensure the instrument is functioning properly. The RPL numbers for the samples are 01-02326 through 01-02335. Work package W57955 will be charged for the analyses.

If you have any questions please call me on 376-3358 or 376-5384.

Concurrence:

*M. W. G. G. G.*  
9-26-01

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: September 26, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 123  
Measurement and test equipment WC38625

Sample ID: 23HC64-12  
Analysis Date: September 25, 2001  
RPL Number: 01-02326

Mole  
Percent Estimate of  
Precision

Argon	0.609 ± 0.01
Carbon Dioxide	0.187 ± 0.004
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.180 ± 0.004
Methane	0.002 ± 0.001
Nitrogen	51.1 ± 0.8
Oxygen	13.4 ± 0.3
Nitrous Oxide	< 0.01 ± 0
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	34.5 ± 0.7
Comments:	

Sample ID: 23HC64-2  
Analysis Date: September 25, 2001  
RPL Number: 01-02327

Mole  
Percent Estimate of  
Precision

Argon	0.002 ± 0.0005
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.314 ± 0.006
Methane	0.003 ± 0.001
Nitrogen	0.49 ± 0.01
Oxygen	0.036 ± 0.001
Nitrous Oxide	0.45 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.7 ± 0.1
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: September 26, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 123  
Measurement and test equipment WC38625

Sample ID: 23HC64-3  
Analysis Date: September 25, 2001  
RPL Number: 01-02328

✓ Mole  
Percent Estimate of  
Precision

Argon	0.003 ± 0.0005
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.295 ± 0.006
Methane	0.004 ± 0.001
Nitrogen	0.48 ± 0.01
Oxygen	0.027 ± 0.001
Nitrous Oxide	0.52 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.7 ± 0.1
Comments:	

Sample ID: 23HC64-4  
Analysis Date: September 25, 2001  
RPL Number: 01-02329

✓ Mole  
Percent Estimate of  
Precision

Argon	0.003 ± 0.0005
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.473 ± 0.009
Methane	0.005 ± 0.001
Nitrogen	0.61 ± 0.01
Oxygen	0.027 ± 0.001
Nitrous Oxide	0.66 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.2 ± 0.1
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: September 26, 200  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 123  
Measurement and test equipment WC38625

Sample ID: 23HC64-5  
Analysis Date: September 25, 2001  
RPL Number: 01-02330

✓  
Mole  
Percent  
Estimate of  
Precision

Argon	0.002 ± 0.0005
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.43 ± 0.009
Methane	0.004 ± 0.001
Nitrogen	0.54 ± 0.01
Oxygen	0.025 ± 0.001
Nitrous Oxide	0.66 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.3 ± 0.1
Comments:	

Sample ID: 23HC64-6  
Analysis Date: September 25, 2001  
RPL Number: 01-02331

✓  
Mole  
Percent  
Estimate of  
Precision

Argon	0.001 ± 0.0005
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.443 ± 0.009
Methane	0.004 ± 0.001
Nitrogen	0.448 ± 0.009
Oxygen	0.015 ± 0.001
Nitrous Oxide	0.74 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	98.3 ± 0.1
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: September 26, 200  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 123  
Measurement and test equipment WC38625

Sample ID: 23HC64-7  
Analysis Date: September 25, 2001  
RPL Number: 01-02332

Mole  
Percent Estimate of  
Precision

Argon	0.002 ± 0.0005
Carbon Dioxide	< 0.001 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.74 ± 0.01
Methane	0.009 ± 0.001
Nitrogen	0.94 ± 0.02
Oxygen	0.022 ± 0.001
Nitrous Oxide	1.05 ± 0.02
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	0.004 ± 0.001
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	97.2 ± 0.1
Comments:	

Sample ID: 23HC64-8  
Analysis Date: September 25, 2001  
RPL Number: 01-02333

Mole  
Percent Estimate of  
Precision

Argon	0.018 ± 0.001
Carbon Dioxide	< 0.01 ± 0
Carbon Monoxide	< 0.01 ± 0
Helium	< 0.001 ± 0
Hydrogen	0.48 ± 0.01
Methane	0.006 ± 0.001
Nitrogen	2.19 ± 0.04
Oxygen	0.401 ± 0.008
Nitrous Oxide	0.69 ± 0.01
Other Nitrogen Oxides	< 0.005 ± 0
C2Hx	< 0.001 ± 0
Other Hydrocarbons	< 0.001 ± 0
Ammonia (estimated)	± 0
Neon	96.2 ± 0.1
Comments:	

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: September 26, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 123  
Measurement and test equipment WC38625

Sample ID: 23HC64-9 ✓  
Analysis Date: September 25, 2001  
RPL Number: 01-02334

	Mole Percent	Estimate of Precision
Argon	< 0.001	± 0
Carbon Dioxide	< 0.01	± 0
Carbon Monoxide	< 0.01	± 0
Helium	< 0.001	± 0
Hydrogen	0.73	± 0.01
Methane	0.008	± 0.001
Nitrogen	0.71	± 0.01
Oxygen	0.009	± 0.001
Nitrous Oxide	0.95	± 0.02
Other Nitrogen Oxides	< 0.005	± 0
C2Hx	< 0.001	± 0
Other Hydrocarbons	0.002	± 0.001
Ammonia (estimated)		± 0
Neon	97.6	± 0.1
Comments:		

Sample ID: 23HC64-10 ✓  
Analysis Date: September 25, 2001  
RPL Number: 01-02335

	Mole Percent	Estimate of Precision
Argon	0.003	± 0.0005
Carbon Dioxide	< 0.01	± 0
Carbon Monoxide	< 0.01	± 0
Helium	< 0.001	± 0
Hydrogen	0.86	± 0.01
Methane	0.008	± 0.001
Nitrogen	0.94	± 0.02
Oxygen	0.047	± 0.001
Nitrous Oxide	1.15	± 0.02
Other Nitrogen Oxides	< 0.005	± 0
C2Hx	0.003	± 0.001
Other Hydrocarbons	0.002	± 0.001
Ammonia (estimated)		± 0
Neon	97.0	± 0.1
Comments:		

## Pacific Northwest National Laboratory

From: 325 Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-3358 / mail slot P7-22  
Date: September 26, 2001  
Subject: Air standards from Finnigan MAT - 271 Mass Spectrometer

Analytical procedure: PNNL - 98523 - 284 Rev. 0  
Laboratory Record Book 56998: Page 123  
Measurement and test equipment WC38625

Accepted values for the composition of air :

	Mole percent
Argon	0.934
Nitrogen	78.08
Oxygen	20.95

Analyzed Values:

Analysis Date: September 26, 2001

	Mole percent
Argon	0.937
Nitrogen	78.02
Oxygen	21.00

Analyzed Values:

Analysis Date: September 26, 2001

	Mole percent
Argon	0.937
Nitrogen	77.91
Oxygen	21.11

Instrument Background:

Background analyses are run daily prior to sample analyses. Trace amounts of hydrogen and/or water in the 0.1 to 0.2 millivolt range were the only species detected. The background spectra is subtracted from each sample spectra.





Project No. \_\_\_\_\_

Internal Distribution

File/LB

Date October 8, 2001

To S.A. Bryan

From S.J. Bos *Stan Bos*

Subject Gas sample analyses

Analyses of ten 23HC69 samples received October 2, 2001 have been completed. A report detailing the analyses is attached. Sample analyses were performed on the Finnigan MAT-271 (M&TE WC38625) quantitative gas mass spectrometer. A performance check of the instrument is run daily, prior to running samples, using high purity nitrogen. Two weekly air standards are also analyzed to ensure the instrument is functioning properly. The RPL numbers for the samples are 02-00004 through 02-00013. Work package W57955 will be charged for the analyses.

If you have any questions please call me on 376-3358 or 376-5384.

Concurrence:

*Ma Shee* 10-10-01

## Pacific Northwest National Laboratory

From: Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-5384 / mail slot P7-22  
Date: October 3, 2001  
Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 126  
Measurement and test equipment WC38625

Sample ID:	23HC69-12	Mole	Estimate of
Analysis Date:	October 02, 2001	Percent	Precision
RPL Number:	02-00004		
Argon	0.002 ± 0.0005		
Carbon Dioxide	< 0.005 ± 0		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.56 ± 0.01		
Methane	0.005 ± 0.001		
Nitrogen	0.75 ± 0.01		
Oxygen	0.018 ± 0.001		
Nitrous Oxide	0.84 ± 0.02		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	< 0.001 ± 0		
Ammonia (estimated)	± 0		
Neon	97.8 ± 0.1		
Comments:			

Sample ID:	23HC69-2	Mole	Estimate of
Analysis Date:	October 02, 2001	Percent	Precision
RPL Number:	02-00005		
Argon	0.004 ± 0.001		
Carbon Dioxide	< 0.005 ± 0		
Carbon Monoxide	< 0.01 ± 0		
Helium	< 0.001 ± 0		
Hydrogen	0.53 ± 0.01		
Methane	0.005 ± 0.001		
Nitrogen	1.10 ± 0.02		
Oxygen	0.025 ± 0.001		
Nitrous Oxide	0.72 ± 0.01		
Other Nitrogen Oxides	< 0.005 ± 0		
C2Hx	< 0.001 ± 0		
Other Hydrocarbons	< 0.001 ± 0		
Ammonia (estimated)	± 0		
Neon	97.6 ± 0.1		
Comments:			

## Pacific Northwest National Laboratory

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 Phone: (509) 376-5384 / mail slot P7-22  
 Date: October 3, 2001  
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To: Sam Bryan

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 Laboratory Record Book 56998 Page 126  
 Measurement and test equipment WC38625

Sample ID:	23HC69-3		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00006	Percent	Precision
Argon		0.002 ±	0.0005
Carbon Dioxide		< 0.005 ±	0
Carbon Monoxide		< 0.01 ±	0
Helium		< 0.001 ±	0
Hydrogen		0.53 ±	0.01
Methane		0.006 ±	0.001
Nitrogen		0.83 ±	0.02
Oxygen		0.025 ±	0.001
Nitrous Oxide		0.82 ±	0.02
Other Nitrogen Oxides		< 0.005 ±	0
C2Hx		< 0.001 ±	0
Other Hydrocarbons		< 0.001 ±	0
Ammonia (estimated)		±	0
Neon		97.8 ±	0.1
Comments:			

Sample ID:	23HC69-4		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00007	Percent	Precision
Argon		0.001 ±	0.0005
Carbon Dioxide		< 0.005 ±	0
Carbon Monoxide		< 0.01 ±	0
Helium		< 0.001 ±	0
Hydrogen		0.60 ±	0.01
Methane		0.006 ±	0.001
Nitrogen		0.76 ±	0.02
Oxygen		0.013 ±	0.001
Nitrous Oxide		0.91 ±	0.02
Other Nitrogen Oxides		< 0.005 ±	0
C2Hx		< 0.001 ±	0
Other Hydrocarbons		< 0.001 ±	0
Ammonia (estimated)		±	0
Neon		97.7 ±	0.1
Comments:			

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Subject: Gas Species Analysis

To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 126  
Measurement and test equipment WC38625

Sample ID:	23HC69-5	Mole	Estimate of
Analysis Date:	October 02, 2001	Percent	Precision
RPL Number:	02-00008		
Argon	0.001	± 0.0005	
Carbon Dioxide		± 0	
Carbon Monoxide		± 0	
Helium	< 0.001	± 0	
Hydrogen	0.470	± 0.009	
Methane	0.004	± 0.001	
Nitrogen	0.49	± 0.01	
Oxygen	0.015	± 0.001	
Nitrous Oxide	0.82	± 0.02	
Other Nitrogen Oxides		± 0	
C2Hx		± 0	
Other Hydrocarbons		± 0	
Ammonia (estimated)		± 0	
Neon	98.2	± 0.1	
Comments:			

Sample ID:	23HC69-6	Mole	Estimate of
Analysis Date:	October 02, 2001	Percent	Precision
RPL Number:	02-00009		
Argon	0.001	± 0.0005	
Carbon Dioxide	< 0.005	± 0	
Carbon Monoxide	< 0.01	± 0	
Helium	< 0.001	± 0	
Hydrogen	0.59	± 0.01	
Methane	0.005	± 0.001	
Nitrogen	0.51	± 0.01	
Oxygen	0.006	± 0.001	
Nitrous Oxide	0.98	± 0.02	
Other Nitrogen Oxides	< 0.005	± 0	
C2Hx	< 0.001	± 0	
Other Hydrocarbons	< 0.001	± 0	
Ammonia (estimated)		± 0	
Neon	97.9	± 0.1	
Comments:			

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To: Sam Bryan

Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 126  
Measurement and test equipment WC38625

Sample ID:	23HC69-7		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00010	Percent	Precision
Argon		0.001 ±	0.0005
Carbon Dioxide		< 0.005 ±	0
Carbon Monoxide		< 0.01 ±	0
Helium		< 0.001 ±	0
Hydrogen		0.73 ±	0.02
Methane		0.009 ±	0.001
Nitrogen		0.80 ±	0.02
Oxygen		0.017 ±	0.001
Nitrous Oxide		0.98 ±	0.02
Other Nitrogen Oxides		< 0.005 ±	0
C2Hx		0.004 ±	0.001
Other Hydrocarbons		0.002 ±	0.001
Ammonia (estimated)		±	0
Neon		97.5 ±	0.1
Comments:			

Sample ID:	23HC69-8		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00011	Percent	Precision
Argon		0.018 ±	0.001
Carbon Dioxide		< 0.005 ±	0
Carbon Monoxide		< 0.01 ±	0
Helium		< 0.001 ±	0
Hydrogen		0.367 ±	0.007
Methane		0.005 ±	0.001
Nitrogen		2.02 ±	0.04
Oxygen		0.319 ±	0.006
Nitrous Oxide		0.73 ±	0.02
Other Nitrogen Oxides		< 0.005 ±	0
C2Hx		< 0.001 ±	0
Other Hydrocarbons		0.002 ±	0.001
Ammonia (estimated)		±	0
Neon		96.5 ±	0.1
Comments:			

## Pacific Northwest National Laboratory

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Analytical procedure : PNNL-98523-284, Rev. 0  
Laboratory Record Book 56998 Page 126  
Measurement and test equipment WC38625

Sample ID:	23HC69-9		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00012	Percent	Precision
Argon	< 0.001	± 0	
Carbon Dioxide	< 0.005	± 0	
Carbon Monoxide	< 0.01	± 0	
Helium	< 0.001	± 0	
Hydrogen	0.87	± 0.02	
Methane	0.011	± 0.001	
Nitrogen	0.67	± 0.01	
Oxygen	0.008	± 0.001	
Nitrous Oxide	1.21	± 0.02	
Other Nitrogen Oxides	< 0.005	± 0	
C2Hx	0.005	± 0.001	
Other Hydrocarbons	0.005	± 0.001	
Ammonia (estimated)		± 0	
Neon	97.2	± 0.1	
Comments:			

Sample ID:	23HC69-10		
Analysis Date:	October 02, 2001	Mole	Estimate of
RPL Number:	02-00013	Percent	Precision
Argon	< 0.001	± 0	
Carbon Dioxide	< 0.005	± 0	
Carbon Monoxide	< 0.01	± 0	
Helium	< 0.001	± 0	
Hydrogen	1.31	± 0.03	
Methane	0.015	± 0.001	
Nitrogen	0.94	± 0.02	
Oxygen	0.010	± 0.001	
Nitrous Oxide	1.55	± 0.03	
Other Nitrogen Oxides	< 0.005	± 0	
C2Hx	0.005	± 0.001	
Other Hydrocarbons	0.007	± 0.001	
Ammonia (estimated)		± 0	
Neon	96.2	± 0.1	
Comments:			

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From: 325 Gas & Isotopic Mass Spectrometry  
Phone: (509) 376-3358 / mail slot P7-22  
Date: October 01, 2001  
Subject: Air standards from Finnigan MAT - 271 Mass Spectrometer

Analytical procedure: PNNL - 98523 - 284 Rev. 0  
Laboratory Record Book 56998: Page 125  
Measurement and test equipment WC38625

Accepted values for the composition of air :

	Mole percent
Argon	0.934
Nitrogen	78.08
Oxygen	20.95

Analyzed Values:

Analysis Date: October 01,2001

	Mole percent
Argon	0.938
Nitrogen	78.06
Oxygen	20.96

Analyzed Values:

Analysis Date: October 01,2001

	Mole percent
Argon	0.936
Nitrogen	77.92
Oxygen	21.11

Instrument Background:

Background analyses are run daily prior to sample analyses. Trace amounts of hydrogen and/or water in the 0.1 to 0.2 millivolt range were the only species detected. The background spectra is subtracted from each sample spectra.

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